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**CLAIMS**

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[Claim(s)]

[Claim 1] The average cluster size of said active species phase is a powder batch with which it is about 20 nanometers or less, and said electrode catalyst particle has the surface area of about 90m<sup>2</sup>/g at least including the primary support particle which has the mean particle diameter said whose support phases are about 10 - 100 nanometers of abbreviation including the active species phase which is a powder batch containing a composite electrode catalyst particle, and said electrode catalyst particle is distributing to a support phase and said support Aigami.

[Claim 2] The powder batch according to claim 1 with which said active species phase has the average cluster size of about 0.5 to about 5 nanometers.

[Claim 3] The powder batch of said active species phase according to claim 1 with which about 50% has the cluster size of about 3 nanometers or less at least.

[Claim 4] The powder batch according to claim 1 with which said active species phase contains a metal.

[Claim 5] The powder batch according to claim 1 with which said active species phase contains a platinum metal.

[Claim 6] The powder batch according to claim 1 with which said active species phase contains a metallic oxide.

[Claim 7] The powder batch according to claim 1 with which said active species phase contains transition-metals oxide.

[Claim 8] The powder batch according to claim 1 with which said active species phase contains manganese oxide.

[Claim 9] The powder batch according to claim 1 with which said electrode catalyst particle has the surface area of about 200m<sup>2</sup>/g at least.

[Claim 10] The powder batch according to claim 1 with which said primary support particle contains carbon.

[Claim 11] The powder batch according to claim 1 with which said primary support particle contains graphite carbon.

[Claim 12] The powder batch according to claim 1 with which said electrode catalyst particle has mean diameter about 10 micrometers or less.

[Claim 13] The powder batch according to claim 1 which has the mean diameter said whose electrode catalyst particle is about 1 micrometer - about 10 micrometers.

[Claim 14] A powder batch according to claim 1 with said almost spherical electrode catalyst particle.

[Claim 15] The powder batch containing said active species phase said whose electrode catalyst particles are about 20 - 40 percent by weight abbreviation according to claim 1.

[Claim 16] The powder batch according to claim 1 with which said electrode catalyst particle has about 40% of voidage at least.

[Claim 17] The powder batch whose average cluster size of said metal active species phase it is the powder batch of a metal-carbon composite electrode catalyst particle, and is about 10 nanometers or less, including the primary carbon particle which is equipped with the metal active species phase which said electrode catalyst particle is distributing to a carbon support phase and said support Aigami, and has the mean diameter said whose support phases are about 20 - 40 nanometers of abbreviation.

[Claim 18] The powder batch according to claim 17 with which said metal active species phase contains a platinum metal.

[Claim 19] The powder batch according to claim 17 with which said metal active species phase contains a platinum metal.

[Claim 20] The powder batch according to claim 17 with which said active species phase contains a metal alloy.

[Claim 21] The powder batch according to claim 17 with which said electrode catalyst powder has the surface area of about 200m<sup>2</sup>/g at least.

[Claim 22] The powder batch according to claim 17 with which said electrode catalyst powder has about 40% of voidage at least.

[Claim 23] The powder batch of said active species phase according to claim 17 with which about 50% has the cluster size of about 3 nanometers or less at least.

[Claim 24] The powder batch whose average cluster size of said metallic-oxide active species phase it is the powder batch of a composite electrode catalyst particle, and is about 10 nanometers or less, including the primary support particle which has the mean particle diameter said whose support phases are about 20 - 40 nanometers of abbreviation including the metallic-oxide active species phase which said electrode catalyst particle is distributing to a carbon support phase and said support Aigami.

[Claim 25] The powder batch according to claim 24 with which said metallic-oxide active species phase contains transition-metals oxide.

[Claim 26] The powder batch according to claim 24 with which said metallic-oxide active species phase contains manganese oxide.

[Claim 27] The powder batch according to claim 24 with which said electrode catalyst particle has the surface area of about 200m<sup>2</sup>/g at least.

[Claim 28] The powder batch according to claim 24 with which said electrode catalyst particle has about 40% of voidage at least.

[Claim 29] It is the approach of manufacturing a composite electrode catalyst particle. The process which generates the globule of aerosol from a precursor liquid, The aforementioned precursor liquid at least The 2nd active species phase precursor is included [ 1st / support phase precursor and ] at least, Process to which said globule is moved in b carrier gas The c aforementioned globule is heated. The approach which said active species phase is distributing to said support Aigami including the process which remove a liquid from this globule, and at least one side of said 1st and 2nd precursors is made to react, and forms a composite electrode catalyst particle.

[Claim 30] The approach according to claim 29 said carrier gas is air.

[Claim 31] The approach according to claim 29 said carrier gas is nitrogen.

[Claim 32] The approach according to claim 29 said heating process includes making the heating zone which has the reaction temperature of about 400 degrees C or less pass said globule.

[Claim 33] The approach according to claim 29 said heating process includes making said globule pass through the heating zone which has the reaction temperature of about 300 degrees C or less.

[Claim 34] The approach according to claim 29 said active species phase is a metal and the aforementioned precursor liquid contains a reducing agent further.

[Claim 35] The approach according to claim 29 said active species phase is a metallic oxide, and the aforementioned precursor liquid contains an oxidizer further.

[Claim 36] The approach according to claim 29 said 1st precursor contains particle carbon.

[Claim 37] The approach according to claim 29 said 1st precursor contains the particle carbon which has the surface area of about 200m<sup>2</sup>/g at least.

[Claim 38] The approach according to claim 29 said 1st precursor contains the particle carbon which has the mean diameter of about 20 - 40 nanometers of abbreviation.

[Claim 39] The approach according to claim 29 the process which generates said aerosol includes atomizing said liquid ultrasonically.

[Claim 40] The approach according to claim 29 the process which generates said aerosol includes passing a NI hydraulic nozzle for the aforementioned precursor liquid.

[Claim 41] It is the manufacture approach of a composite electrode catalyst particle. The process which forms a particle carbon precursor and the liquid precursor which contains the 1st active species phase precursor at least, Process which generates the globule of aerosol from the b aforementioned liquid precursor The process which heats the globule of said aerosol at the conversion temperature of about 400 degrees C or less among c spray

drier, and forms an electrode catalyst particle is included. The approach from which said 1st precursor is changed into the active species phase currently distributed to said support Aigami.

[Claim 42] The approach according to claim 41 said liquid precursor contains a reducing agent.

[Claim 43] The approach according to claim 41 said liquid precursor contains an oxidizer.

[Claim 44] The approach according to claim 41 said conversion temperature is about 300 degrees C or less.

[Claim 45] The approach according to claim 41 said particle carbon precursor has the surface area of about 600m<sup>2</sup>/g at least.

[Claim 46] The approach according to claim 41 the process which generates said aerosol includes making a NI hydraulic nozzle pass said liquid precursor.

[Claim 47] the manufacture approach of the particle containing a polymer phase -- it is -- a -- the process which forms the liquid content precursor which contains the 1st precursor component and polymer emulsion at least, The process which generates the globule of precursor aerosol from the liquid content precursor of b above, The particle manufacture approach including the process which heats the globule of the precursor aerosol of c above, removes a liquid from this globule, and forms said particle.

[Claim 48] The particle manufacture approach according to claim 47 that said 1st precursor component contains a particle precursor.

[Claim 49] The particle manufacture approach according to claim 47 that said 1st precursor component contains particle carbon.

[Claim 50] The particle manufacture approach according to claim 47 that said 1st precursor component contains the particle carbon which has mean diameter about 100 nanometers or less.

[Claim 51] The particle manufacture approach according to claim 47 that said 1st precursor component contains the particle carbon which has the surface area of about 25m<sup>2</sup>/g at least.

[Claim 52] The particle manufacture approach according to claim 47 that said 1st precursor component contains the particle carbon which has the surface area of about 90m<sup>2</sup>/g at least.

[Claim 53] The particle manufacture approach according to claim 47 that said polymer is a fluorocarbon polymer.

[Claim 54] The particle manufacture approach according to claim 47 that said polymer is a tetrafluoroethylene fluorocarbon polymer.

[Claim 55] The particle manufacture approach according to claim 47 that said heating process includes heating said aerosol in temperature of about 400 degrees C or less.

[Claim 56] The particle manufacture approach according to claim 47 that said heating process includes heating said aerosol in temperature of about 300 degrees C or less.

[Claim 57] The particle manufacture approach according to claim 47 that said liquid precursor contains the 2nd precursor component.

[Claim 58] The particle manufacture approach according to claim 47 that said liquid precursor contains a carbon precursor and a platinum precursor.

[Claim 59] The particle manufacture approach according to claim 47 which contains further the 2nd precursor component in which said 1st precursor component contains amorphous carbon, including graphite carbon.

[Claim 60] a) Current collector arranged on a gaseous diffusion layer Electrode assembly which is equipped with the electrode catalyst bed arranged on the b aforementioned current collector, and decreases including the carbon particle and electrode catalyst particle which said electrode catalyst bed is distributing over the whole polymer matrix as the hydrophobicity of said polymer matrix separates from said current collector.

[Claim 61] The electrode assembly according to claim 60 with which said gaseous diffusion layer contains a porosity tetrafluoroethylene fluorocarbon polymer.

[Claim 62] The electrode assembly according to claim 60 with which said current collector is equipped with the metaled piece of-like [ long picture ].

[Claim 63] The electrode assembly according to claim 60 with which said current collector is equipped with the piece of-like [ long picture ] of a metal with a width of face of about 100 micrometers or less.

[Claim 64] The electrode assembly according to claim 60 with which said carbon particle has mean diameter about 10 micrometers or less.

[Claim 65] The electrode assembly according to claim 60 with which said polymer matrix contains a tetrafluoroethylene fluorocarbon polymer.

[Claim 66] The electrode assembly according to claim 60 with which said polymer matrix decreases as the

amount of said tetrafluoroethylene polymer in said polymer matrix separates from said current collector including a tetrafluoroethylene fluorocarbon polymer.

[Claim 67] The electrode assembly according to claim 60 with which said electrode catalyst particle contains a carbon complex particle.

[Claim 68] The electrode assembly containing the platinum metal active species which said electrode catalyst particle is distributing to a carbon support phase and said support Aigami according to claim 60.

[Claim 69] The electrode assembly according to claim 60 with which said electrode catalyst particle has mean diameter about 5 micrometers or less.

[Claim 70] The electrode assembly according to claim 60 which said current collector and said electrode catalyst bed double, and has the average thickness of about 100 micrometers or less.

[Claim 71] The electrode assembly according to claim 60 with which said the greater part of carbon particle in said polymer matrix is arranged near said current collector.

[Claim 72] a) Gaseous diffusion layer Current collector arranged on the b aforementioned gaseous diffusion layer Electrode assembly with which the concentration of a carbon particle [ as opposed to an electrode catalyst particle in said inclination stratum functionale ] decreases with the distance from said current collector including the inclination stratum functionale arranged at the c aforementioned current collector bottom, including a carbon particle and an electrode catalyst particle.

[Claim 73] The electrode assembly according to claim 72 with which said gaseous diffusion layer contains a porosity tetrafluoroethylene fluorocarbon polymer.

[Claim 74] The electrode assembly according to claim 72 with which said current collector is equipped with the metaled piece of-like [ long picture ].

[Claim 75] The electrode assembly according to claim 72 with which said current collector is equipped with the piece of-like [ long picture ] of a metal with an average width of face of about 100 micrometers or less.

[Claim 76] The electrode assembly according to claim 72 with which said carbon particle has mean diameter about 10 micrometers or less.

[Claim 77] The electrode assembly according to claim 72 with which said inclined layer contains a tetrafluoroethylene fluorocarbon polymer.

[Claim 78] The electrode assembly according to claim 72 with which said inclined layer is equipped with hydrophobic inclination.

[Claim 79] The electrode assembly according to claim 72 with which said electrode catalyst particle contains a carbon complex particle.

[Claim 80] The electrode assembly according to claim 72 with which said electrode catalyst particle has mean diameter about 10 micrometers or less.

[Claim 81] The electrode assembly according to claim 72 with which said current collector and said inclination layer have the average thickness of about 50 micrometers or less.

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[Translation done.]



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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]****(Background of invention)**

1. Field of invention This invention relates to the product and device incorporating the manufacture approach of particle ingredients, such as electrode catalyst powder for energy device production, and such powder, and powder. This powder is preferably manufactured by carrying out spraying conversion (spray conversion) of the precursor to a particle ingredient.

**[0002]**

2. Explanation of related technique By the growing demand to the electric vehicle by a burden being increasingly placed on the natural resource in which the appearance of the electron device of the size which it can have in a hand by the pocket formula and playback are impossible, immediate development of a highly efficient and economical power system is called for. The energy using the energy storage device and fuel cell which use a cell and which were improved needs to be generated for such a power system.

**[0003]**

A cell may be classified into primary (charge is impossible) and a secondary (charge is possible) cell. Metal-air cells, such as Zn-air, Li-air, and aluminum-air, an alkaline cell, and a lithium cell are contained in the primary cell of the usual type. Nickel-cadmium NIUMU, nickel hydrogen, and a lithium ion battery are contained in the rechargeable battery of the usual type.

**[0004]**

One type of the metal-air cell which brings about many advantages which the contention force has is a zinc air battery, and is based on the redox couple of oxygen and zinc. A zinc air battery adsorbs oxygen from ambient atmosphere air, and operates by returning oxygen in the cathode called an air electrode using an oxygen reduction catalyst. When oxygen is returned, a zinc metal oxidizes. The reaction of the zinc-air alkaline cell under discharge is as follows.

**[0005]**

Cathode:  $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$  Anode plate:  $2Zn \rightarrow 2Zn^{2+} + 4e^-$  Whole:  $2Zn + O_2 + 2H_2O \rightarrow 2Zn(OH)_2$  The stack of the air electrode is carried out to the zinc electrode by turns, and it is usually packed by the container wide opened to air. When a cell discharges, oxygen is returned to  $O_2^-$  in cathode, and a zinc metal oxidizes to coincidence in an anode plate at  $Zn^{2+}$ . Since Zn can be electrodeposited from an electrolyte water solution in order to reproduce an anode plate, a zinc air battery may also be a rechargeable battery like being a primary cell.

**[0006]**

There are safety, long operating time, and lightweight nature in the advantage of the zinc-air rechargeable battery which excels the cell system in which other charge is possible. This cell operates with one atmospheric pressure excluding a toxic ingredient. 2 to 4 hours of most lithium ion batteries which can be charged -- comparing -- them -- 10 to 14 hours -- long -- time amount actuation is carried out, and they can be saved for a long period of time, without discharging. Since the zinc air battery is lightweight, power density (a unit weight or output per volume) is large, and this is ideal for the application of a portable type.

**[0007]**

However, the two main problems about a zinc-air rechargeable battery are that full power is restricted and that charge nature / cycle life is not repeatedly good. The big outputs for the cell manufacturer who is going to fill

the high demand of the newest electronic equipment are the main areas of interest. The present zinc air battery can take out 450 W/kg from about 200 which makes it possible to usually use this cell for a certain specific low-power output laptop and other portable type devices which need low-power output comparatively. However, most portable type electron devices of laptop one and others need the cell of the output of big level rather than it can supply the present zinc air battery. It is thought that the main reasons nil why the output of a zinc air battery is small are inefficiently [ the catalytic reaction which returns oxygen with an air electrode ] related. That it is hard to contact a catalyst, a catalyst, and the partial fine structure of the contiguity carbon circumference reduce the effectiveness of oxygen reduction. For example, Py . N . Ross et al. (P. N.Ross et al.), Journal of the Electrochemical Refer to Society, Vol.131, and pg.1742 (1984).

[0008]

Repetition charge nature is also one problem of a zinc air battery. The cycle life of this cell is short and the engine performance falls considerably after the charge cycle not more than about 200 times or it. It is thought that the shortness of the cycle life of a zinc air battery is related to the catalyst currently too used with the air electrode. Capacity specifically falls by corrosion of the carbon currently used as an electrode catalyst by these systems, therefore it is thought that a charging time value comes to decrease.

[0009]

It is used for current and a primary (charge being impossible) alkali zinc air battery operating the hearing aid and other devices which need a low current consistency over a long period of time. The zinc air battery of hearing aid includes air cathode and a zinc system anode plate again. Electrode catalyst powder is formed in air catholyte, and changes the oxygen in air into the hydroxide ion in catalyst. Next, the inside of an alkaline electrolyte is conveyed to the hydroxide ion through a separator in an anode plate, and it reacts with zinc there, generates zincate (zincate,  $\text{Zn}(\text{OH})_4^{2-}$ ) ion and zinc ion ( $\text{Zn}^{2+}$ ), and separates an electron. The electrode catalyst powder with which air cathode was improved will extend the life of such a primary cell with sufficient convenience.

[0010]

In addition to the amelioration in an energy storage, the amelioration in environment-friendly economical energy generation is called for. A fuel cell is the electrochemical device which can transform the energy of a chemical reaction into electrical energy, without polluting as a matter of fact again, without making it burn. Since a fuel cell transforms chemical energy into electrical energy, sending a chemical reaction object to a fuel cell continuously, it differs from a cell. The potential is zero when a fuel cell is turned OFF. As a result, a fuel cell is usually used for manufacturing the source of continuous electrical energy, and competes with other gestalten of continuous electrical energy production of a combustion engine, nuclear electric power generation, a coal combustion electric power plant, etc. The fuel cell various type is classified according to the electrolyte used with a fuel cell. The five main types of a fuel cell are alkali, a melting carbonate, a phosphoric acid, a solid acid ghost and the proton exchange film (PEM), or a solid-state polymer fuel cell.

[0011]

One of the important requirements is performing catalyst-conversion to the electrical energy of a reactant efficiently deterministically for these energy devices. The serious failure over changing such a device quotient business on a large scale is lack of the very efficient electrode catalyst for these translation processes.

[0012]

One example of the fuel cell which uses an electrode catalyst for a chemical reaction is a proton exchange film fuel cell (Proton Exchange Membrane Fuel Cell, PEMFC). A PEMFC stack includes the membrane electrode assembly (membrane electrode assembly, MEA) of hundreds including the cathode which consists of for example, carbon crosses, respectively, and an anode plate. An anode plate and cathode have put between membranous both sides the proton exchange film which has a catalyst bed. When hydrogen is supplied to an anode plate and oxygen (air) is supplied to cathode, an output arises. In the reaction in which a catalyst is usually carried out by the platinum system catalyst of an anode plate catalyst bed, hydrogen is ionized and produces a proton and an electron. A proton is conveyed to the catalyst bed of the membranous opposite side (cathode) through the proton exchange film, platinum or a platinum alloy carries out the catalyst of the reaction of oxygen to a proton, and catalyst another there and usual generate water. A reaction can be written as follows.

[0013]

Anode plate:  $2\text{H}_2 \rightarrow 4\text{H}^{++} + 4\text{e}^-$  Cathode:  $4\text{H}^{++} + 4\text{e}^- + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$  Whole:  $2\text{H}_2 + \text{O}_2 \rightarrow$  The electron generated in

the 2H<sub>2</sub>O anode plate is sent to cathode through the electrical circuit which supplies power.

A point of argument important for the decision target which has to inquire in order to make commercialization of a fuel cell successful is the engine performance and operation life of the cost of a cel, and a cel. Improvement in power density is deterministically important, and, on the other hand, the bigger potential efficiency for a standing application is required of an automotive application. From the standpoint of the cost of a fuel cell, the present fuel cell stack makes each of an anode plate and cathode support about 4mg [ per square centimeter ] platinum, and MEA including a platinum-electrode catalyst is used for it. About 19g [ per kilowatt ] platinum is required of the typical cel engine performance of 0.42W per square centimeter (0.42 W/cm<sup>2</sup> broken 8 mgPt/cm<sup>2</sup>). The platinum metal is very expensive, and in order for these cels to have implementability economically, the remarkable cost reduction of an electrode catalyst is required for it. However, since there is also a strong request which is going to depend on existence of a platinum-electrode catalyst and is going to raise the engine performance of a cel, it is not suitable solution to reduce the amount of noble metals.

[0014]

The main technical challenges are raising the engine performance of cathode with the air as an oxidizer. Acid electrolyte either alkalinity or medium is used, and the platinum metal-electrode catalyst for oxygen reduction is used by the PEM fuel cell, the alkali fuel cell, the hybrid fuel cell, and others.

[0015]

Some processes are included in the usual synthesis method of the electrode catalyst powder which has active species on a support ingredient. The solution with which the precursor of active species is contained is infiltrated into the suitable high surface area catalyst support (for example, an alumina, a titania, a silica, or carbon) for the 1st. Sufficient contact time for adsorption of an active species precursor to take place and for a precursor finish adhering to a carrier surface again at homogeneity is taken. Next, a catalyst is dried in order to remove a solvent from about 2 over 12 hours, for example at the temperature of 100 to 120 degrees C. Next, a catalyst is heated at 600 degrees C from an elevated temperature and 400 degrees C of usual in air, and a precursor is changed into active species. Usually, an oxide catalyst does not need the further processing.

[0016]

Generally the fine structure of a presentation and complex powder is not enough controlled by said approach as a result. The surface area of mol follow G and electrode catalyst powder is the property of having important effect deterministically for the engine performance of a catalyst. Mol follow G defines pack density, and surface area defines the type and number based on [ that active species is formed during electrode catalyst composition ] surface adsorption. It is the main failures for future development of energy storage and a production device that the fundamental property of electrode catalyst powder is uncontrollable.

[0017]

In this technical field, the preparation approach of a noble-metals electrode catalyst ingredient is learned. U.S. Pat. No. 4,052,336 of VAMMON photographs (VanMontfoort et al.) indicates the process which prepares an activity precious metal catalyst on carbon support, and prepares palladium etc. for example, on carbon by returning an oxide or a hydroxide to a metal by making a metal salt adsorb on carbon and making an oxide or a hydroxide generate from a metal salt. Carbon support contains the porosity activity carbon particle which has the particle size of the large range from a thing smaller than 1 micrometer to 60 micrometers. This catalyst contains the noble metals of about 0.1 to about 15 percentage by weight. It is indicated that noble metals have adhered on carbon support with the gestalt of minute microcrystal (kristallite) with whenever [ per 1g of noble metals / catalytic activity / large ].

[0018]

JARAN's and others (Jalan et al.) U.S. Pat. No. 4,136,059 indicates the manufacture approach of a platinum particle [ activity / target / for using it with a fuel cell electrode / electrochemistry ]. This particle mixes a platonic chloride (chloroplatinic acid) and a sodium dithionite (sodium dithionite) underwater, and is manufactured by considering as the colloid dispersing element absorbed by the support ingredient (an example, carbon black).

[0019]

U.S. Pat. No. 4,482,641 of WENABAGU (Wennerberg) indicates the high surface area porosity activity carbon matrix containing a metaled homogeneity dispersing element. This ingredient carries out spray drying of a carbon precursor and the metal precursor, forms a particle, and is manufactured by pyrolyzing the particle by

which spray drying was carried out next to the bottom of alkali-metal hydroxide existence under inert gas. The desirable heating approach for a pyrolysis process is heating using a microwave heating method. A metallic crystal is about 5 to 30Å in particle size, and is arranged on the activity carbon which has cage structure.

[0020]

Men's past his prime (Ozin et al.) U.S. Pat. No. 4,569,924 indicates the carbon-metal catalyst which has active metals, such as silver which adhered to carbon support with the gestalt of the small cluster of zero \*\* (zero-valent). This catalyst is manufactured by evaporating a metal in an organic liquid solvent under low vapor pressure conditions so that a metal may dissolve in a solvent. Next, a complex contacts a solvent to carbon so that it may be further spread in the pore of carbon on a carbon front face. This carbon particle supports the metal of 0.1 to 15 percentage by weight.

[0021]

Tamra's and others (Tamura et al.) U.S. Pat. No. 4,652,537 indicates the manufacture approach of a useful catalyst, although a carbon monoxide is changed into a carbon dioxide. The activated carbon is contacted in the solution of platinum chloride (IV) hydro acid, the absorbed platinum chloride (IV) hydro acid is returned to platinum with a reducing agent, and disassembling a superfluous reducing agent is included in this process. Preferably, even if there are few these catalysts per [ which was activated ] 1g of carbon, they contain about 6mg platinum. The activated carbon particle has about 0.4 to about 10-millimeter diameter of average granulation. Wart [0022]

ITOU's and others (Itoh et al.) U.S. Pat. No. 4,970,128 indicates the support platinum alloy electrode catalyst for acid electrolyte fuel cells. A platinum alloy contains platinum, iron, and copper. This electrode catalyst has the initial activity and the life superior to conventional platinum or other multicomponent alloy electrode catalysts. U.S. Pat. No. 5,489,563 of brands (Brand et al.) indicates the platinum / cobalt / chromium alloy catalyst settled on carbon support from the nitrate.

[0023]

U.S. Pat. No. 4,970,189 of Citrus tachibana (Tachibana) indicates the porosity carbon ingredient containing a metal with which the mean diameter distributed by the matter of the quality of carbon contains fine metal particles 1 micrometer or less. Mixing a metallic oxide with the organic substance, carbonizing an oxide, and changing into metal particles is included in this approach. The metal of about 5 to 50 percentage by weight is contained in this catalyst.

[0024]

KEKKU's and others (Keck et al.) U.S. Pat. No. 5,068,161 indicates the electrode catalyst ingredient suitable for using with a phosphoric-acid fuel cell. This ingredient contains an alloy with other elements, such as platinum, titanium, chromium, manganese, iron, cobalt, nickel, copper, a gallium, a zirconium, or a hafnium. Support of a platinum alloy is 20 to 60 percentage by weight, and the electrochemical area of an alloy is larger than about 35m<sup>2</sup>/g.

[0025]

Weiss's and others (Weiss et al.) U.S. Pat. No. 5,120,699 indicates the catalyst which contains the platinum of 0.01 to 5 percentage by weight in graphite support. Graphite support has about 1 to 600-micrometer particle size distribution. A catalyst ingredient has a long life, when used for a hydrogenation reaction.

[0026]

U.S. Pat. No. 5,453,169 of call storms (Callstorm et al.) indicates the electrode catalyst containing the glassy carbon with which particle size includes an about 1 to 20-nanometer graphite crystal.

[0027]

HAZU's and others (Hards et al.) U.S. Pat. No. 5,501,915 indicates the porous electrode suitable for using on the particle carbon into which the proton conductivity polymer was infiltrated with a solid-state polymer fuel cell including the precious metal catalyst distributed to altitude.

[0028]

Generally a presentation and the fine structure of an electrode catalyst ingredient are not fully controlled by said approach as a result, and the dispersibility and surface area of active species on a carbon front face are not fully controlled by it, either. Furthermore, the alloy presentation of the platinum/ruthenium used for reduction of oxygen with a fuel cell is not manufactured in the way which is consistent and is reproducible. It is the main failures for development of a more efficient electrode material that a powdered fundamental property is

uncontrollable.

[0029]

Offering the large approach of the application range which it is difficult to manufacture using the existing manufacture approach, or the property of powder, such as an impossible particle size and surface area, and pore structure, is controlled, and can manufacture electrode catalyst powder with a various presentation will be that there is an advantage. If such powder can manufacture in large quantities in a continuous way substantially, there will be especially an advantage. A layer will also be that offering devices with which it was improved, such as a cell whose engine performance improved thinly, and a fuel cell, has an advantage.

[0030]

(Detailed description)

Generally this invention relates to powder useful to manufacture of an energy device of useful electrode catalyst powder etc., and the method of manufacturing this powder by the fuel cell and the cell. One desirable operation gestalt of this invention is related with the composite electrode catalyst powder for carrying out the catalyst of the useful chemical reaction to a cell and a fuel cell. This invention relates also to the new device produced using these powder. There are fuel cells, such as a PEM fuel cell, as an example. Another example is a metal-air primary cell which uses air cathode for returning oxygen. The ingredient by this invention can be formed in a film with sufficient convenience using the direct writing deposition technique for forming peculiar structure.

[0031]

According to 1 operation gestalt, a composite electrode catalyst particle is targetted for this invention. On these specifications, composite electrode catalyst powder or particles are things which contain the phase of the 1st active species in each particle at least, such as a metal currently distributed on the phase of support, such as carbon or a metallic oxide, or a metallic oxide. The complex powder of this invention consists of a particle containing both not the mere physical mixture of a different particle but an active species phase, and a support phase. Possible [ changing the presentation of a particle component independently ], if required because of a specific application, various combination of carbon, a metal, a metal alloy, a metallic oxide, a mixed metallic oxide, organometallic compounds, and these partial pyrolysates can be made. One operation gestalt of this invention is aimed at the composite electrode catalyst particle which has two or more sorts of different ingredients as active species. As one example, the combination of Ag supported by carbon and MnOx is useful for some electrode catalyst applications, and it gets. Other examples which consist of much active species are a porphyrin, a partial decomposition porphyrin, and the mixture of Co and CoO. Although carbon is an ingredient desirable as a support phase, other ingredients, such as a metallic oxide, are useful and it is sold at some electrode catalyst applications.

[0032]

According to 1 operation gestalt of this invention, electrode catalyst powder contains a metal-carbon composite electrode catalyst particle. A metal-carbon composite electrode catalyst particle contains the active species which is distributed to carbon support Aigami and which consists of the 1st metal phase at least. A metal layer can contain any metals and especially the desirable metal will be based on the powdered application. A metal phase may be a metal alloy with which the 1st metal is alloyed with one sort or two or more alloy elements. On these specifications, the intermetallic compound between two or more sorts of metals is contained in vocabulary called a metal alloy. Metal-carbon-electrode catalyst powder can also contain two or more sorts of metals distributed on support as an independent phase again.

[0033]

A platinum metal and noble metals especially Pt, Ag, Pd, Ru and Os(es), and these alloys are contained in a metal desirable as electrode catalyst-active species. The metal chosen from the combination of nickel, Rh, Ir, Co, Mo, W, V, Nb, aluminum, Ta, Ti, Zr, Hf, Zn, Fe, Cu, Ga, In, Si, germanium, Sn, Y, La, lanthanide metals, and these metals or the group of an alloy can be included in a metal phase again. Pt and other metals, for example, an alloy with Ru, Os, Cr, nickel, Mn, and Co, are contained in the desirable metal alloy used according to this invention. These desirable by the way are Pt-Ru used in a hydrogen anode plate, and Pt-Cr-Co used in oxygen cathode.

[0034]

Another desirable operation gestalt of this invention is aimed at the metallic-oxide-carbon composite electrode catalyst particle containing the metallic-oxide active species currently distributed on carbon support. The phase

of metallic-oxide active species can be chosen from the transition-metals oxide which has an oxygen deficiency in those crystal structures most preferably from the oxide of transition metals and the transition metals which exist as oxides of desirable various oxidation states.

[0035]

For example, the metallic oxide currently distributed is an oxide of Au, Ag, Pt, Pd, nickel, Co, Rh, Ru, Fe, Mn, Cr, Mo, Re, W, Ta, Nb, V, Hf, Zr, Ti, or aluminum metal, and it deals in it. Especially the desirable metallic oxide by this invention is manganese oxide ( $MnO_x$  and  $x$  are 1 to 2). The activity phase currently distributed can contain the solid solution or the multiple oxide of the mixture of a different oxide, and two or more sorts of different metallic oxides. A metallic oxide may be a stoichiometry, may be nonstoichiometric, and may be the mixture of the oxide of one sort of metals which have a different oxidation state. A metallic oxide may be amorphous.

[0036]

For some applications, such as a metal-air rechargeable battery, the metallic oxide which can perform reduction/oxidation reaction by change of the oxidation state of the metal contained in an oxygen deficiency metallic oxide and a metallic oxide is contained in the example of the electrode catalyst ingredient by this invention which can carry out the catalyst of reduction and the oxidation reaction. A certain compound is various functions and has many properties (attribute) to one compound. It is not necessarily required to distribute such an oxide on support.

[0037]

For example, according to this invention, a perovskite phase oxide can be used as an electrode catalyst, and this oxide offers electrode catalytic activity, high surface area, and electric conductivity.  $La_{1-x}Sr_xFe_{0.6}Co_{0.4}O_3$  ( $x$  is 0 to 1) and  $La_{1-x}Ca_xCoO_3$  ( $x$  is 0 to 1) are contained in the example of such a perovskite phase oxide. Especially one desirable metallic-oxide electrode catalyst by this invention is an oxygen-deficiency cobalt-nickel oxide and  $CoxNi_{1-x}O_z$ , and this is useful as an electrode of a metal hydride cell. In this kind of other metallic oxide, A by  $AB_2O_4$  Mg, [ a general formula ] calcium, Sr, Ba, Fe, Ru, Co, nickel, Cu, Pd, Pt, Eu, It is chosen from divalent metals or these combination, such as Sm, Sn, Zn, Cd, and Hg. The spinel as which B is chosen from trivalent metals or these combination, such as Co, Mn, Re, aluminum, Ga, In, Fe, Ru, Os, Cr, Mo, W, Y, Sc, and a lanthanide metal, is contained. Manganese oxide, nickel oxide, cobalt oxide, ferrous oxide, titanium oxide, a zirconium dioxide, a zinc oxide, indium oxide, indium tin oxide, an oxidation gallium and a metal gallate, ruthenium oxide and a metal ruthenate, chromic oxide, molybdenum and a tungsten, oxidation copper and a copper content perovskite phase metallic oxide, a vanadium oxide, a niobium, and a tantalum are contained in other useful metallic oxides.

[0038]

The catalyst of another class in which it is useful and deals by this invention is guided from the molecularity compound which is distributing to support Aigami or does not have a support phase. Although the example of such an ingredient carries out the catalyst of the reduction to  $OH^-$  of  $O_2$ , it is a metalloporphyrin complex which oxidizes between oxidation of  $OH^-$ . This kind of thing is suitable for fuel cells, such as a primary cell and an alkali fuel cell. The metal Pori Phi Lynne complex of Co, Fe, Zn, nickel, Cu, Pd, Pt, Sn, Mo, Mn, Os, Ir, and Ru is contained in this group. Other metal ligand complexes may be activity in these catalyst-oxidation and a reduction reaction, and can manufacture these by the approach indicated by this specification. Such a metal ligand can be chosen from the kind of the  $N_4$ -metal chelate represented with a porphyrin, tetraaza annulene (tetraazaannulene), a phthalocyanine (phtalocyanine), and other chelating agents. In a certain case, there is activity to which an organic ligand carries out the catalyst of reduction and the oxidation reaction. although a ligand comes out as it is and it is activity as it comes out so in the case of a porphyrin ring system as it is and may be in it, they can be made to be able to react partially during heat treatment, and another chemical species in which are activity too and it deals can also be made to generate in a catalyst-reaction in a certain case An example is a resultant guided from a porphyrin or other organic compounds.

[0039]

It is thought that carbon is required for the reduction to  $OH^-$  of  $O_2$ , and it is participating in the reduction to the hydroxide ion of a peroxide. Gay-fullerene, hetero-fullerene, and a carbon nanotube system ingredient are contained in other carbon system active species.

[0040]



In order to obtain various performance characteristics for a specific application about the composite electrode catalyst particle of this invention, the property of the primary particle which constitutes a secondary support phase and a secondary support phase, and active species is independently controllable.

[0041]

The powder of a metal and a metal alloy (an intermetallic compound is included) is useful to an electrode, especially the anode plate of a certain specific cell again. LaNi<sub>5</sub>, La-nickel-Co-aluminum, Nd-Ce-nickel-Co-aluminum, and V-Ti-Cr-nickel are contained in the example of such metallic compounds.

[0042]

In order to produce the energy device component by this invention in addition to electrode catalyst powder, other fine powder is useful. Insulating materials for membrane separation, such as a charge of supporting material, a hydrophobic ingredient, a conductive ingredient, and a dielectric, are in these. For example, metals, such as silver (Ag) and nickel (nickel), can be used for the current collector of a cell.

[0043]

According to 1 operation gestalt of this invention, particles, such as a carbon particle or an electrode catalyst particle A polymer, For example, TEFLON (Trademark) etc. -- a tetrafluoroethylene (TFE) fluorocarbon polymer (IAIDEYUPONDOUNU blue mussel (E. I. duPont de Nemours) [the U.S. Delaware Wilmington (Wilmington) whereabouts]) Or a sulfonation perfluoro hydrocarbon polymer (for example, it NAFION(s) (trademark)) It is embellished with a polymer by coating of the particle by proton conductivity polymers, such as an IAIDEYUPONDOUNU blue mussel (E. I. duPont de Nemours) [the U.S. Delaware Wilmington (Wilmington) whereabouts]. For example, in order to form a hydrophobic layer in an energy device so that it may be indicated below, a polymer qualification carbon particle can be used. Hydrophobicity can be adjusted by adjusting the ratio of TEFLON (trademark) and carbon. In order to build a polymer modified electrode catalyst particle, TEFLON (trademark) can also be made to adhere on an electrode catalyst particle for a certain application.

[0044]

The aforementioned composite electrode catalyst powder contains the secondary support phase which consists of floc of smaller primary particles, such as carbon which supports active species, or a metallic oxide. In order to form a secondary support phase, two or more sorts of primary particles are mixable. As an example, in order to form a secondary support phase, two or more sorts of particle carbon (for example, amorphous and graphite) can be mixed. Two sorts of particle carbon can have different performance characteristics combined in order to raise the engine performance of a catalyst.

[0045]

It is one advantage of this invention for the presentation of an electrode catalyst particle to be uniform and to get. The uniformity coefficient of an ingredient is not obtained depending on the conventional formation approaches, such as precipitation from a liquid, in many cases. However, it is also possible to give presentation inclination intentionally in an electrode catalyst particle. For example, being also higher than near [ the ] a core and a low thing are possible for the active species concentration in a complex particle on the front face of a support phase, and it can acquire the inclination equivalent to presentation change of 10 to 100 percentage by weight. When making a particle adhere by direct writing deposition, it is possible for a particle to continue having the mol follow G on those structures, therefore to use the functionality of presentation inclination so that it may be indicated below by this specification.

[0046]

Furthermore, since this electrode catalyst particle is usually a high grade, it can raise electrode catalytic activity. Many of impurities of the electrode catalyst powder of the conventional technique originate in a precursor and a surfactant. As for the surface impurity of the electrode catalyst particle of this invention, in measurement by X-ray photoelectron spectroscopy (XPS), it is possible for it to be conveniently smaller than 1 atomic ratio.

[0047]

The gestalt of the desirable carbon for crystalline support active species is amorphous. Since the desirable carbon of a support metal like Pt has the returned desirable carbon front face which does not have a surface water acid radical in distribution of Pt substantially, it is crystalline carbon. It is desirable too that it is crystalline carbon support in Support MnOx. Preferably, the crystallinity of the primary particle which constitutes a support phase is controlled through selection of the ingredient chosen to a specific application.



Graphite carbon is desirable for the long-term operation stability of a fuel cell and a cell. Amorphous carbon is desirable when the smaller microcrystal size for support active species is desirable.

[0048]

The consistency as the whole secondary support phase (namely, condensed primary particle) in a complex particle is related to the voidage of a support phase. As for the available (for example, it opened) voidage of a composite electrode catalyst particle, it is desirable that it is about 5 to 98%, and it is about 40% at least more preferably. Also being able to control [ and ] the pore volume distribution of a secondary support phase, an average pore diameter is about 10 to about 100 nanometers, for example, about 10 to 20 nanometers, preferably. Big voidage is convenient although chemical species frequent a secondary structure object quickly. It is printing techniques, such as ink jet deposition which needs to make a particle suspend for a long period of time, that grain density is small again, and it makes it possible to make a particle suspend more easily. As for the consistency of aerogel carbon or an aerogel metallic oxide, as an example, it is possible for it to be much smaller than 1 g/cm<sup>3</sup>.

[0049]

Condensation of an electrode catalyst particle may affect properties of a powder batch, such as the dispersibility of the powder to the liquid used in order to make a particle adhere. Therefore, as for condensation of the particle of a powder batch, it is desirable that it is the minimum.

[0050]

It is one advantage of this invention that the configuration of an electrode catalyst particle is also almost spherical. That is, the configuration of a particle does not have a notch or irregularity preferably. A spherical particle can be made to adhere with sufficient convenience using various techniques including direct writing deposition (direct write deposition), and a spherical particle can form a thin layer with large pack density.

[0051]

furthermore, the complex electrode catalyst by this invention -- desirable -- at least -- about 10m<sup>2</sup>/g -- more -- desirable -- at least -- about 25m<sup>2</sup>/g -- more -- desirable -- at least -- about 90m<sup>2</sup>/g -- moreover, it has the surface area of about 600m<sup>2</sup>/g at least much more preferably. Surface area is measured using the BET nitrogen adsorption process which usually contains the specific surface area of the pore which can use in a catalyst particle and which shows powdered surface area. High distribution of active species and \*\*\*\*\* quantity surface area make catalytic activity increase generally.

[0052]

according to 1 operation gestalt of this invention -- a composite electrode catalyst particle -- carbon support -- a carrier surface top -- desirable -- at least -- the active species of about 1 percentage by weight -- more -- desirable -- at least -- the active species of about 5 percentage by weight -- furthermore, it contains with the catalyst-active species of 10 percentage by weight much more preferably. In 1 operation gestalt, this particle contains the active species phase of about 20 - 40 percentage by weight abbreviation. Bringing about the property of an electrode catalyst in which such presentation level has an advantage most for many applications was found out. However, the desirable level of the active species currently distributed on carbon support will be based on the type of the total surface area of carbon, and active species, and the powdered application. Probably, the percentage of the active species of the front face must be small in order for the carbon support with small surface area to make surface concentration of active species the same compared with support with much [ surface area / surface area is large and ] support of active species.

[0053]

As for the average magnitude of the active species phase currently distributed to support Aigami, it is desirable that it is that in which the particle contains the cluster of the two or more small single crystals or microcrystal called a cluster by both on these specifications. In 1 operation gestalt, an active species cluster pitch diameter is about 10 nanometers or less preferably, and is about 5 nanometers or less more preferably, and is about 3 nanometers or less much more preferably. In 1 operation gestalt, average cluster size is about 0.5 to 5 nanometers. another operation gestalt of this invention -- setting -- at least -- about 50% of number -- more -- desirable -- at least -- about 60% of number -- moreover, the active species cluster of at least 70% of number has the particle size of about 3 nanometers or less much more preferably. Thus, also conveniently compared with the complex powder containing the active species phase which has a bigger cluster, the property of composite electrode catalyst powder which has a small microcrystal cluster of a catalyst is improving. The

approach of this invention can improve [ control of degree of crystallinity ] convenience by controlling reaction temperature and/or the residence time.

[0054]

When active species contains a metal, the oxidation state of the metal of a metal phase is preferably close to zero, i.e., a pure metal. It is thought that a higher oxidation state is harmful for the activity of electrode catalyst powder. The approach of this invention enables [ conveniently or ] control which was excellent in the metal oxidation state.

[0055]

The electrode catalyst powder of this invention usually has the often controlled particle size. According to 1 operation gestalt of this invention, volume mean particle diameter is about 100 micrometers or less, and is about 20 micrometers or less preferably, and is 10 micrometers or less more preferably. Furthermore, it is desirable that it is about 0.3 micrometers at least, and it is about 0.5 micrometers at least more preferably, and volume mean particle diameter is about 1 micrometer at least much more preferably. On these specifications, mean particle diameter is a median particle diameter (d50). The powder batch which has a mean diameter within the desirable limits indicated on these specifications enables formation of a thin electrode catalyst bed advantageous to manufacturing peculiar energy devices, such as a cell by this invention, and a fuel cell.

[0056]

A secondary support phase, a primary particle, and the particle size distribution of active species are important for opting for the catalyst engine performance, and according to this invention, they can control these enough. Comparatively narrow particle size distribution is desirable so that a particle can be made to adhere, without making it get it blocked through a narrow orifice for a secondary support phase and a film can be formed. For example, it is desirable that about 50 percents by volume are [ of a particle ] twice [ about / less than ] the particle size of volume mean particle diameter at least, and it is more desirable that about 75 percents by volume are [ of a particle ] twice [ about / less than ] the particle size of volume mean particle diameter at least. Particle size distribution may be bimodal (bimodal) one or TORIMODARU (trimodal) which can raise pack density with sufficient convenience.

[0057]

The process indicated by this specification, i.e., the powder manufactured by spraying conversion, may contain some flocs of a spherical particle. The particle of micron size builds loose floc with those big surface energy in many cases. Such loose floc can be distributed by processing of applying a supersonic wave in a liquid medium, or sifting. The particle size distribution indicated on these specifications is measured by mixing a powder sample with a surfactant in media, such as water, and applying a short-time supersonic wave by either the ultrasonic bath or the horn. An ultrasonic horn supplies sufficient energy for making a primary spherical particle distribute loose floc. Next, light scattering measures the particle size distribution of a primary particle in a MICROTRAC particle-size measuring instrument (Honeywell industrial automation and control (Honeywell Industrial Automation and Control) [the U.S. Pennsylvania photograph Washington (Fort Washington) whereabouts]) etc. Since this is the simulation of the particle distribution in liquid media, such as a paste used for making a particle adhere to a device, or a slurry, it offers the standard which was excellent about the useful property of powdered distribution. Thus, the particle size referred to at this specification expresses the particle size after distributing loose floc.

[0058]

Setting like 1 voice, this invention offers the approach of preparing an electrode catalyst powder batch. A liquid precursor is changed into the gestalt of aerosol, and a liquid is removed from the globule in aerosol so that the desirable particle which is in a distributed condition next may be formed. Although an electrode catalyst powder batch is usually manufactured by dryness, the powder after manufacture can be changed into the wet conditions in a paste or a slurry etc.

[0059]

The manufacture approach of the composite electrode catalyst powder by this invention is called spraying processing, spraying conversion, or a spraying pyrolysis in this specification, and, generally includes the following processes. That is, they are the process which offers the liquid precursor containing the precursor of a support phase (an example, carbon), and the precursor of active species, the process which forms the suspension object (suspension) which atomizes a precursor and consists of a globule of a liquid precursor, and the process

which a liquid is removed [ process ] from a liquid precursor globule and makes powder generate. The precursor of a support phase is not required of the electrode catalyst which is not supported. Usually, at least 1 component of a liquid precursor is chemically changed into a powdered desirable component. According to this invention, desiccation of a precursor and conversion to catalyst-active species are performed by combining with sufficient convenience at one process, and removal of a solvent and the conversion to the active species of a precursor essentially take place to coincidence. things and \*\* with short reaction time -- this enables it to control distribution of the active species on support, the oxidation state of active species, and the degree of crystallinity of active species. The approach of this invention can make the structure of the mol follow G and active species of a catalyst which leads to improvement in the catalyst engine performance by changing the type of reaction time, temperature, and a support ingredient, and the type of a precursor.

[0060]

One mode with the approach of this invention more important for a detail is in the condition which fully contacted the front face of a primary particle where the precursor of an active species phase constitutes a support phase, and I hear that a support electrode catalyst particle is formed, and there is.

[0061]

On a primary support particle front face, I hear that an active species precursor reacts quickly, and another, important mode of the approach by this invention has it. Since the generation reaction of active species occurs by very short time amount, growth of a big active species cluster is suppressed, and migration of the active species cluster on a carrier surface decreases. An active species precursor is preferably put to reaction temperature high for active species generation the time for about 10 or less seconds about 600 or less seconds preferably [ it is more desirable and / about 100 or less seconds and one layer of twists ]. The approach to which an active species precursor is made to react is indicated in a detail below.

[0062]

Another peculiar mode of the spraying processing by this invention is coincidence formation of a secondary support phase of carbon. Generating a secondary support phase as a result of formation of the globule under spraying processing, and desiccation, the property of primary support particles, such as particle size, particle size distribution, and surface area, influences the property of this support phase.

[0063]

It is made to relate to the attribute from which some differ, and grouping of the spraying art for the electrode catalyst manufacture by this invention can be carried out. The thing (as opposed to the direction of the main gas stream), i.e., the horizontal system, or perpendicular system of the following [ attributes / these ], the class (for example, an immersion ultrasonic device, an ultrasonic nozzle, and a NI hydraulic nozzle --) of atomizer the class (for example, a laminar flow without mixing and a turbulent flow without mixing --) of a single pressurization fluid and flow The counterflow of a globule, concurrent [ of elevated-temperature gas ] and a globule, and gas or interflow, a gas heating method There is a class (a cyclone, a bag house, and electrostatic \*\*\*\*\* descend (settling)) of for example, (the combination of an elevated-temperature system wall surface, elevated-temperature gas installation, elevated-temperature gas, and an elevated-temperature wall surface, the plasma or flame), and powder uptake system etc.

[0064]

The spraying processing by 1 operation gestalt of this invention leaves the precursor solution (for example, the colloid carbon for Pt/C electrode catalyst powder manufacture and  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ ) which is atomized and forms a globule. a globule lets the heating zone which a solvent evaporates, and a precursor reacts and generates a desirable ingredient pass -- having -- this desirable ingredient -- the filter top from the flow of gas -- or uptake is carried out with a cyclone. When a globule is in a heating zone, it decomposes and a precursor is crystallized to a product particle. Catalyst phase microcrystal size is controllable by control of the residence time to which a particle stops at the temperature of a heating zone, and a heating zone.

[0065]

For example, the electrode catalyst powder of a metal / carbon, and a metallic oxide/carbon can be prepared by leaving the drainage system precursor liquid which consists of colloid carbon and a metal salt which dissolved. Carbon remains as it is, and it can control the processing temperature of a precursor globule so that a metal salt precursor decomposes. The outline which shows generation of Pt / carbon-electrode catalyst particle is shown in drawing 1 .

[0066]

The 1st process of a process is evaporation of a solvent (usually water), a globule is heated and the particle of the dry solid content and a metal salt is obtained. Some approaches of telling heat to a particle are possible, and a level elevated-temperature wall surface tubular reactor, a spray drier, and a perpendicular tubular reactor can be used. The plasma, a flame, laser, and other reactors can be regarded as these deformation gestalten. A metal precursor is disassembled by whether a particle is made into an elevated temperature, or it puts on a certain specific temperature for a long time. By using the spraying transformation method of this invention, the degree of crystallinity of metal particles and distribution which could control the temperature and time amount which are exerted on a particle, therefore were supported by carbon again are also controllable.

[0067]

The method of generating of a precursor globule does effect important for the property of the last electrode catalyst powder like an aerosol generating rate. The breadth of particle diameter and the diameter distribution (PSD) of a particle (globule) and the atomization rate of a specific fluid are contained in the property decided by the generator. When extreme, by a certain generator, a fluid cannot be atomized by addition of a moderate particle because of skill or hyperviscosity.

[0068]

In order to atomize the flow of supply containing a suspension particle like carbon, some atomization approaches exist, and it has an advantage and a disadvantageous point, respectively. Other approaches learned for ultrasonic transducer (usually vibration frequency of 1-3MHz), ultrasonic nozzle (10-150kHz), and NI hydraulic-nozzle, the pressure atomizer, and this technical field by such approach.

[0069]

In 1 operation gestalt, the scale-up of an immersion supersonic-wave transducer can be performed based on arranging many piezo electric crystals side by side in a fluid. The scale-up of a nozzle system can be carried out by whether the nozzle of a bigger capacity is chosen, or the number of units which are used by making it juxtaposition is increased. Usually, the particle built with a nozzle is larger than what is built with an ultrasonic atomizer. It depends for particle size also on a quantity of gas flow again. By the flow rate of a fixed fluid, the diameter of a grain to which airstream is made to increase becomes small, and the reduction in airstream enlarges particle size. It is difficult to change particle size without changing the flow rate of a liquid or airstream. However, a NI hydraulic nozzle can process the liquid of the large volume from per time amount rather than an ultrasonic atomizer.

[0070]

Although a fluid is atomized by the immersion supersonic-wave transducer, two kinds of fundamental disk configurations, a plane, and the punctiform source can be used. In a plane source configuration, the thin film of a liquid has spread on the oscillating front face, and a stationary wave occurs by the node decided by some physical properties containing vibration frequency, the viscosity of a fluid, surface tension, and a consistency. In a punctiform source configuration, since ultrasonic energy is centralized on the point of a certain distance on a source front face, it can use on deeper fluid level. Concentration of this energy makes the source (fountain) of jet of the cone form which aerosol generates from there. A globule is formed of a cavitation (cavitation) process in the tip of the stationary wave formed on the front face of the source of jet. Carrier gas blows the source of jet, it is accompanied to gas and aerosol is sent to another actuation units, such as a particle-size decollator (impactor (impactor)) or a reactor (furnace). Usually, from an ultrasonic nozzle, a disk-type transducer can be operated with high vibration frequency, and can build a particle with a more small median particle diameter. However, these types of atomizer is difficult to atomize a hyperviscous fluid or a fluid with many particle additions. The immersion supersonic-wave transducer reactor system is shown in KODASU's and others (Kodas et al.) U.S. Pat. No. 6,103,393, and this whole patent is used for this specification by reference.

[0071]

An ultrasonic spraying nozzle has some advantages which endure a single or a NI hydraulic nozzle. The main advantages are that the rate of spraying which leaves a nozzle is small, and that there is no related flow of gas. The energy of high vibration frequency is used for an ultrasonic nozzle atomizing a fluid. Vibration of a high frequency is generated in the center of a nozzle with a piezoelectric transducer crystal. The point that a transducer pours in energy is a node whose lateral displacement to produce is min. The edge of a nozzle is the point of quadrant wavelength and this is an anti--node. In this anti--node, lateral displacement is max. The

outlet edge of a nozzle is much smaller than an inlet-port edge. Lateral displacement is proportional to the relative molecular mass of the ingredient in an anti--node. Since the atomization edge of a nozzle is much smaller than housing behind a nozzle, vibration is amplified at the atomization edge. The nozzle of various orifice dimensions and the diameter of an orifice is marketed so that enlarging or contracting of the system can be carried out to various production capacity. Generally, a high vibration frequency nozzle is more small physically, and its capacity of flow is smaller than the nozzle which builds a smaller globule and operates with low vibration frequency. I hear that the diameter of a grain which enlarges the path of a nozzle becomes large, and the fault of this system about enlarging or contracting has it. If a specific particle size is required, the maximum production rate per nozzle will be then set up. Probably, another nozzle or a package of a production unit is needed in order to attain a desirable production rate, when desirable production is over the maximum production rate of the nozzle.

[0072]

The configuration on the front face of atomization defines the form and breadth of a spraying pattern. The shape of atomization nozzle surface type of some types including a cone form, a micro spray form, and a flat form is marketed. A cone atomization front face brings about the maximum atomization capacity, and gives a big spraying envelope. Although a flat atomization front face brings about the flow of the almost same amount as a cone form, the path of the whole spraying is restricted. A micro spray atomization front face has a very small flow rate, and is for [ which needs a thin spraying pattern ] applications. These nozzles are desirable for the configuration which needs that the flow of the gas accompanying a globule is the minimum.

[0073]

The particle carbon suspension often used for manufacture by the spraying conversion by this invention is related with atomization, and produces the problem of shoes. An immersion supersonic-wave atomizer recycles suspension through a generating chamber, and suspension will become deep if time amount passes. Furthermore, the liquid of a certain rate is atomized without including suspension colloid. Another problem which encounters when using an immersion supersonic-wave transducer is coating of the transducer disk by the particle which will happen if time amount passes. Finally, the generating rate from carbon suspension is very slow in an immersion supersonic-wave transducer. This has a cause in the energy absorbed or reflected by the suspension particle at least partially.

[0074]

As for an immersion supersonic-wave transducer, there is less carbon than 40wt(s)% in the last electrode catalyst desirable to a precursor constituent with few particle carbon contents for example, and it has it than 10wt(s)% much more preferably [ it is more desirable, and is fewer than 20wt(s)%, and ]. [ less ] They are desirable again to any ingredient products formed not from a particle precursor but from the dissolved precursor.

[0075]

\*\*\*\*\* and others has used the both sides of an ultrasonic spraying nozzle and an immersion supersonic-wave transducer, in order to manufacture a Pt/C electrode catalyst according to this invention. The conditions (temperature and residence time) of the reactor used in order to form a catalyst were essentially the same. The catalyst built using two technique had a similar physical characteristic and electrochemical activity. The yield at the time of using an ultrasonic spraying nozzle transducer was 40% - 60% of usual [ of a generation rate theoretical for loss on the wall surface as a result of the big diameter of a globule, and descent ]. The ultrasonic nozzle (a SONO-tech (Sono-Tek) markets) (120kHz) which gives the minimum particle size was used, and the generation rate of the range of 1-2g per hour was obtained. Although the bigger atomization rate is possible, increasing the flow rate of the liquid which lets a nozzle pass does not make the generation rate in a horizontal tubular elevated-temperature wall surface reactor increase with this nozzle. An additional ingredient will only adhere on a furnace tube.

[0076]

Some configurations for introducing into the flow of carrier gas the aerosol built with the nozzle were examined at the horizontal tubular elevated-temperature wall surface furnace. The yield of a process was improved from 40% of a theoretical generation rate to 60% by changing the geometry of an inlet port, the flow rate of carrier gas, and the flow rate of a precursor. In case the great portion of loss introduces aerosol into a furnace, it is generated. By contrast, the immersion supersonic-wave system which has nine transducers had only the

generation rate of about 1-0.4g which hit up for 1 hour. Said generation rate can be measured with the generation rate in the nine same transducer systems of the metal simple substance guided from the dissolved precursor which are usually 10g per hour. The small generation rate in a metal carbon precursor constituent is because atomization of carbon suspension does not work in an immersion ultrasonic device.

[0077]

A NI hydraulic nozzle is a usual means to perform aerosol spraying, and is typically used for much industrial use with the spray drying process. The big shearing force generated when low-speed liquid flow meets with the flow of high-speed gas atomizes. I hear that the particle-size property of aerosol is dependent on the flow rate of gas, and the direct result of this interaction has it. Therefore, the property of a particle is unrelated to the flow rate of carrier gas, and is not acquired. For this reason, the loss of a particle which is not desirable the rate of the particle when going away from a generation zone may be quite large, and according to a collision may arise. It may be needed that aerosol is larger than a pattern characteristic again and the minimum value which has the magnitude of a reactor so that a nozzle may usually be left in a cone form and the loss on the wall surface of a system which is not desirable may be prevented for this.

[0078]

The NI hydraulic nozzle is shown in drawing 2. This NI hydraulic nozzle 100 contains the central opening 102 for leading a liquid precursor to a chamber. When a liquid precursor is sprayed from the central opening 102, two outside openings 104 and 106 turn the jet of air or another gas to the flow of a liquid precursor, and are drawn. Atomization is attained by the big shearing force generated when low-speed liquid flow meets with the flow of high-speed gas. It depends for the particle-size property of aerosol on the flow rate of gas.

[0079]

Therefore, a technique which is different in electrode catalyst manufacture in order to be the flow and the product of supply which various atomization techniques for a spraying translation process are possible, and are different is desirable.

A level elevated-temperature wall surface tubular reactor can heat the flow of gas to desirable temperature. Energy is told to a system by keeping the boundary in a reactor wall surface constant, and the maximum temperature of gas is wall surface temperature. The heat transfer in an elevated-temperature wall surface reactor should happen through the whole gas. The buoyancy automatically generated within a level elevated-temperature reactor helps this migration. This mixing helps to raise the radial homogeneity of the flow of gas again. Active mixing is that gas is passive or assistance to which heat transfer is made to increase again.

[0080]

By changing the residence time slightly, the maximum temperature and the maximum heating rate of flow which enter are controllable independently. The heating rate of the flow which enters is controllable using the furnace of many zones.

[0081]

Desirable use of the level elevated-temperature wall surface reactor by this invention is building a product particle (secondary structure object) with a particle size smaller than about 5 microns, and descent of a particle did not cause important loss in this case. A disadvantageous point is being unable to atomize particle carbon well in immersion supersonic-wave atomization. This technique is desirable at a product with many metaled amounts of support corresponding to there being few carbon contents, and this reason is enough for it for atomization to enable economical manufacture in this case.

[0082]

In 1 operation gestalt, when there are very few additions of carbon, a level elevated-temperature wall surface reactor can be used with an immersion supersonic-wave transducer. In another operation gestalt, a level elevated-temperature wall surface reactor can be used with a NI hydraulic-nozzle atomizer. Since this technique can atomize particle carbon as opposed to a product with a particle size smaller than 5 microns, it is desirable to the flow of supply containing the carbon of a high level. Main un-arranging [ of this technique ] to a particle smaller than 5 microns are that aerosol is thin (there are few amounts of products per volume of gas), and makes this technique the powder manufacture approach which costs require.

[0083]

A level elevated-temperature wall surface reactor can be used with an ultrasonic nozzle (horn) atomization technique. Atomization of particle carbon is possible for this technique. Main un-arranging are big diameters of



a globule which lead to loss of the ingredient in the wall surface and other front faces of a reactor, and makes this technique the powder manufacture approach which costs require.

[0084]

The spraying translation process which consists of spray driers is the desirable approach of mass production method of the electrode catalyst by this invention. However, in almost all spray driers, since the highest inlet temperature is usually restricted by about 316 degrees C (600 degrees F), an elevated temperature required for reduction of platinum cannot be acquired. Therefore, using such spraying conversion system for manufacture of an electrode catalyst was not proposed in front of this invention.

[0085]

A single fluid, a NI hydraulic nozzle, and a rotating-disc atomizer are contained in a useful atomizer with a spray drier. The desirable approach for carrying out spray drying of the particle carbon content precursor of this invention is a NI hydraulic nozzle. An edge is covered with a dry material and a rotating-disc atomizer needs frequent cleaning and an intermittent activity. Although a single hydraulic nozzle can be used, in order to acquire the same particle size distribution, a bigger liquid flow rate is needed.

[0086]

The useful concurrent spray drier by this invention is shown in drawing 3 . A spray drier 200 contains the atomization gas line 203 for atomizing the precursor supply line 202 and supply liquid for sending a liquid precursor in the desiccation chamber 204. A liquid precursor is distributed to a globule through the spraying nozzles 206, such as a NI hydraulic nozzle shown in drawing 2 . Dry air is introduced into the topmost part of a chamber 204 through the elevated-temperature gas inlet 208. It dries and uptake of the globule is carried out to a cyclone 212.

[0087]

In the aforementioned explanation about the basic component of a spray drier, it should be cautious of precursor mixture actually receiving chemical conversion during spray drying. For example, manganese precursors, such as potassium permanganate, are changed into manganese oxide. The final phase and final oxidation state of manganese oxide are deterministically [ for the electrode catalyst-activity of the obtained powder ] important. It can be said that the powder with which electrode catalytic activity differs is obtained by slight modification of reaction temperature and a precursor presentation.

[0088]

In order to acquire the electrode catalyst of high quality, it was advantageously found out by this invention that comparatively low conversion temperature can be used. As for reaction temperature, it is desirable that it is about 400 degrees C or less, and it is 250 degrees C or less preferably [ it is more desirable and / 300 degrees C or less and one layer of twists ]. Furthermore, as for reaction temperature, it is desirable that it is about 100 degrees C at least, and it is about 150 degrees C at least preferably. If reaction temperature is raised exceeding 400 degrees C, the superfluous surfactant which remains on powder and may poison an oxide active site is removable. However, if there will be few amounts of the surfactant in a precursor solution even if there is this, it is not usually required.

[0089]

There are two, concurrent and interflow, in a spray drier as a general class. In a concurrent spray drier, elevated-temperature gas is introduced from the topmost part of a unit, and a globule is generated by the NI hydraulic nozzle. Even if the temperature to which a particle is put with a concurrent dryer is high, it is the temperature of an outlet. By some designs, although an elevated temperature is more possible for outlet temperature, it is usually restricted to about 200 degrees C. Furthermore, since a particle touches [ the beginning of a time amount-temperature curve ] an elevated temperature most at the lowest temperature and the last, the surface diffusion of a precursor and the possibility of condensation are large, therefore disassembly of a precursor is more difficult compared with disassembly of the precursor distributed good.

[0090]

More desirable spraying conversion system is based on arrangement of an interflow spray drier. An interflow system introduces elevated-temperature gas from the topmost part of a unit, and generates a precursor globule near the pars basilaris ossis occipitalis in the upward source of jet. Since a particle is driven away to the topmost part of a unit by this, then it falls with gas and it flows and returns downward again, compared with a concurrent configuration, the residence time of a particle becomes long. The temperature which a particle touches is more



high compared with a concurrent spray drier. Since most spray driers cannot reach conversion of the salt of some precursors used at the higher temperature which is the need, this is important.

[0091]

There are few platinum or platinum alloys, for example, these conditions are advantageous to composition of an electrode catalyst which supports Pt to 50wt(s)%, or the alloy of Pt system on carbon. It is possible for it to be sufficient elevated temperature for Pt system precursor to decompose attainment temperature at an interflow spray drier (for example, for 250 degrees C and 300 degrees C). In these spray driers, a maximum temperature is inlet temperature, and outlet temperature is lower than the one half of inlet temperature. Therefore, an electrode catalyst particle reaches for a short time comparatively at a maximum temperature, and, for this reason, the intra plant transfers (migration) or surface diffusion of a serious precursor is impossible. After the sudden rise to this elevated temperature enabling quick conversion of a metal or a metallic-oxide precursor, then reaching a maximum temperature, since the temperature of a spray drier falls quickly, "the local express cold (pseudo quench)" happens. Thus, the temperature profiles similar to "a sudden rise (spike)" are electrode catalyst support front faces, such as carbon, and are advantageous to the metal or metallic-oxide cluster often distributed generating. This is desirable again in other combination of the metal supported on various support, or a metal oxide catalyst.

[0092]

According to another operation gestalt of this invention, a hybrid perpendicular elevated-temperature wall surface / elevated-temperature gas pipe-like reactor can be used. Since the settling velocity of the particle of the micron size generated by this method is small in the case of the fine particles generated by the immersion supersonic-wave transducer disk, descent of a particle does not become a problem. However, all liquid precursors are not well atomized like a carbon colloid carbon solution using an ultrasonic transducer disk. Therefore, different atomization techniques, such as an ultrasonic spraying nozzle or a NI hydraulic nozzle, are desirable, and these tend to generate the larger globule of a larger particle size than about 5-10 microns. In order to avoid descent loss, the aforementioned perpendicular system is required for this.

[0093]

The hybrid perpendicular system is shown in drawing 4 , and the advantage of both an elevated-temperature wall surface system and the mass-in bigger nozzle than that for building big globule rather than it makes total volume increase desiccation system using elevated-temperature air installation is used. The radial dimension of a desirable system is larger than a standard horizontal system again. It is needed in order that the longer furnace of a suitable output (3 times of a usually thermodynamic request) may ensure suitable time amount-temperature hysteresis. This system is preferentially used at sufficient elevated temperature, in order to disassemble many molecularity precursors (to 700 degrees C). Elevated-temperature resistance stainless steel is a desirable coil. The elevated-temperature gasket of a water cooling type is desirable. Before powdered uptake will be performed in order to make growth of a cluster into the minimum if elevated-temperature desiccation / reaction occurs, cooling or quenching quickly is desirable. Another desirable mode is being able to use elevated-temperature gas (to 700 degrees C) independently of an elevated-temperature wall surface as a desiccation/reaction means. This elevated-temperature gas can offer all types desirable from reducibility to an oxidizing quality of ambient atmosphere.

[0094]

If drawing 4 is referred to, a nozzle 402 will send a precursor into the topmost part of a system like a concurrent spray drier. Carrier gas is beforehand heated by the temperature by which it was controlled from about 700 degrees C to 1000 degrees C, and then is introduced into the topmost part of a system through the cylindrical dispersing element 404 immediately under a nozzle 402. Next, elevated-temperature carrier gas and a globule flow down through the perpendicular elevated-temperature wall surface reactor tubing 406 which can control wall surface temperature. After it is dried and changed, next it is cooled and uptake of the powder is carried out to a cyclone or a bag filter 408. With this configuration, the generation rate is increasing by permitting generation of a bigger globule (it has a big settling velocity) with loss decreasing in comparison with a horizontal system compared with all other spraying conversion system. This system will bring about a generation rate larger a single figure than a horizontal system, if other techniques are used. Another advantage of a perpendicular system is that the time amount-temperature hysteresis of aerosol is doubled with any useful profiles in practice.

[0095]

This hybrid system can be operated in the three modes. The 1st is as an elevated-temperature wall surface tubular reactor. The 2nd is concurrent flow elevated-temperature gas desiccation similar to a spray drier. The 3rd mode uses an elevated-temperature wall surface and elevated-temperature gas. In order to maintain desirable particle temperature, the flow of an elevated temperature or low temperature gas can be introduced in front of a furnace or in the back.

[0096]

The 25kHz nozzle (a maximum of 12.5 Lph) of :mass which compared operation using the nozzle of three types in a hybrid system, a cone spraying pattern; inside capacity nozzle of 48kHz (a maximum of 4.5 Lph), and flat cylindrical spraying pattern; and the 120kHz nozzle (a maximum of 1.3 Lph) of low capacity, a cone spraying pattern.

[0097]

A tip generates the globule which is too large for past [ breadth ] and a low vibration frequency supersonic-wave nozzle drying the spraying pattern of the nozzle of a cone form in sufficient time amount in a tubular system. Even if inside and a mass nozzle reduce the throughput of a liquid (low vibration frequency), in order to evaporate them completely, they generated the too large globule. The highest gas and wall surface temperature were able to attain evaporation of a perfect liquid by the liquid flow rate smaller than 0.8Lph using the small 120kHz nozzle. Therefore, in 1 desirable operation gestalt, a flat high vibration frequency supersonic-wave nozzle is used. This type of nozzle builds quite narrow mono-modal (monomodal) particle size distribution and a comparatively small globule, and this evaporates and changes and serves as electrocatalysis.

[0098]

The flow rate of the greatest precursor liquid was determined by investigating extent of evaporation. In contrast with the alien system of the same particle size, a hybrid reactor furnace can dry and change 5% of the weight of the carbon suspended in water a maximum of 700 g/hr according to a nozzle and the particle size of a subsequent globule.

[0099]

The result described here is water 5-% of the weight SHAWINIGAN. It carried out with the BLACK solution. The particle which has the surface area of 100m<sup>2</sup>/g [ a maximum of ]2/g was generated by operation at the temperature of hot carrier gas and a 600-degree C reactor wall, and on the other hand, when the temperature of a reactor wall was lowered to 400 degrees C, surface area became small to about 55m<sup>2</sup>/g. When the temperature of a reactor wall was lowered to 200 more degrees C, the surface area of about 35m<sup>2</sup>/g was generated.

[0100]

Although the carbon which has hot carrier gas and was collected by the cyclone and which was processed on the 400-degree C perpendicular system had the surface area of 36.5m<sup>2</sup>/g, on the other hand, the carbon which has hot carrier gas and was collected by the back cyclone filter bag and which was generated at 400 degrees C had the surface area of 72.0m<sup>2</sup>/g. This observation shows that the collector efficiency from which cyclone collection and back cyclone filter bag collection differ exists to the powder which has different surface area. Furthermore, in a cone nozzle, small quantity is taken with a gas installation screen and a reactor tube wall.

[0101]

Therefore, the 1st process in manufacture of the electrode catalyst particle by this invention is forming the liquid precursor of a particle. In the case of the supported electrode catalyst powder, a liquid precursor contains the precursor of both active species and a support phase. By choosing a precursor appropriately, it becomes possible to generate the particle which has the often controlled chemical property and a physical characteristic.

[0102]

In order to generate the metal carbon composite electrode catalyst particle by this invention, a precursor solution contains at least one metal precursor. A metal precursor can be considered as the matter of the liquid phase or solid phase. As for a metal precursor, it is desirable that it is the metal-containing compound which dissolved in the liquid solvent of liquid feed stocks, such as a salt. For example, a precursor solution can contain a metaled nitrate, a chloride, a sulfate, a hydroxide, or carboxylate. However, the salt of a chloride may bring about a harmful catalyst property in connection with the passage of time. A metal precursor receives one or more chemical reactions, when it is heated, and is changed into a metal condition and the electrode catalyst particle of this invention is formed. By adding a hydrochloric acid etc., it may be desirable to make a precursor

solution into acidity and to raise solubility.

[0103]

The desirable catalytic activity-ized metal by 1 operation gestalt of this invention is platinum (Pt). A platinic chloride ( $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ ), a tetra-amine platinum (II) nitrate ( $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ ), and hydroxo platinic acid ( $\text{H}_2\text{Pt}_6(\text{OH})$ ) are contained in the desirable precursor of the platinum metal by this invention. Pt nitrate, Pt amine nitrate, and  $\text{Na}_2\text{PtCl}_4$  etc. is contained in other platinum precursors. The platinic chloride is meltable in water and, as for a solution, it is advantageous to maintain low viscosity. Since  $\text{H}_2\text{Pt}(\text{OH})_6$  is comparatively changed into a platinum metal at low temperature, it is advantageous.

[0104]

According to other operation gestalten of this invention, palladium is desirable as a catalytic activity metal. A palladium precursor contains inorganic Pd salt for a palladium (II) chloride ( $\text{PdCl}_2$ ), a palladium (II) nitrate ( $\text{Pd}_2(\text{NO}_3)_2$ ),  $\text{H}_2\text{PdCl}_4$ , or  $\text{Na}_2\text{PdCl}_4$ . Complicated Pd salts, such as  $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$  or  $\text{Pd}(\text{NH}_3)_2(\text{OH})_2$ , Pd carboxylate, etc. are useful.

[0105]

Silver (Ag) is useful as a catalytic activity metal. The mineral salt containing Ag nitrate ammine complex (Ag-nitrate ammine complex), Ag-carboxylate, and Ag-OKISA rate is used for silver. Silver carbonate ( $\text{Ag}_2\text{CO}_3$ ), a silver nitrate ( $\text{AgNO}_3$ ), and silver acetate ( $\text{AgOOCCH}_3$ ) are especially desirable.

[0106]

There are an osmium (Os) and copper (Cu) in other useful catalytic activity metals. Mineral salt, such as  $\text{OsCl}_3$ , can be used for an osmium. Copper acetate (II), ( $\text{Cu}(\text{OOCCH}_3)_2$ ), a copper(II) chloride ( $\text{CuCl}_2$ ), a copper nitrate (II), ( $\text{Cu}(\text{NO}_3)_2$ ), perchloric acid copper (II) and ( $\text{Cu}(\text{ClO}_4)_2$ ), and copper carboxylate can be used for copper.

[0107]

In order to generate the electrode catalyst powder containing a metallic oxide including the supported metallic oxide and the metallic oxide which is not supported, the precursor of a metallic oxide must be contained in the precursor solution. A nitrate, a chloride, a hydroxide, a halogenide, a sulfate, phosphate, carboxylate, an oxyrate, and the mineral salt containing a carbonate can be used for a metallic oxide as a precursor including the oxide of Au, Ag, Pt, Pd, nickel, Co, Rh, Ru, Fe, Mn, Cr, Mo, Re, W, Ta, Nb, V, Hf, Zr, Ti, or aluminum. A metale oxide can be used also as a precursor to the metallic oxide of the last powder.

[0108]

In a desirable metallic oxide, as a chromic-acid ghost, especially  $\text{K}_2\text{Cr}_2\text{O}_7$ , Cr carboxylate, As a manganic acid ghost, And oxalic acid chromium;  $\text{KMnO}_4$ , Mn nitrate, It is supposed as a tungstic-acid ghost that it is  $\text{Na}_2\text{WO}_4$  and a  $\text{W}_2\text{O}_3$ ; molybdic-acid ghost. As  $\text{K}_2\text{MoO}_4$  and  $\text{MoO}_2$ ; cobalt oxide Mn acetate, Mn carboxylate, Mn ARUKOSHIKIDO, and  $\text{MnO}_2$ ; Co amine complex, Co carboxylate, And cobalt oxide; Cu amine complex, Cu carboxylate, and copper oxide are contained as a nickel oxide as nickel amine complex, nickel carboxylate, and nickel oxide; and a copper acid ghost.

[0109]

According to the desirable operation gestalt of this invention, the precursor of a metal or a metallic oxide is a cation precursor. A cation precursor is a precursor whose metals (for example, platinum) are a part of cation chemical species of a precursor salt. For example, the desirable cation precursor of a platinum metal is a tetra-amine platinum (II) nitrate (tetraamine platinum(II) nitrate).

[0110]

In order to generate the complex powder which has a carbon support phase, a precursor solution also contains at least one carbon precursor. A carbon precursor can be used as organic precursors, such as polykaryotic carboxylic acids, such as carboxylic acids, such as a terephthalic acid, isophthalic acid, trimesic acid, and trimellitic acid, a benzoic acid, polycarboxylic acid, or a naphthoic acid, or polykaryotic polycarboxylic acid. An organic precursor can react according to a device like a degree type.

[0111]

$a\text{M}(\text{NO}_3)_n + b(\text{C}_x\text{H}_y\text{O}_z)_m \rightarrow \text{MaCb}$  By using a liquid organic carbon precursor, amorphous carbon is usually obtained. This is not desirable to application of almost all the electrode catalyst. As for a carbon support precursor, it is desirable that it is distribution of a suspension carbon particle. Carbon particles are additives, such as a surfactant which makes suspension stability, and can be suspended in water. The carbon particle used

as a precursor is a primary particle which constitutes a secondary support phase.

[0112]

a primary carbon precursor particle -- at least -- about 20m<sup>2</sup>/g -- more -- desirable -- at least -- about 80m<sup>2</sup>/g -- it is further more preferably desirable about 250m<sup>2</sup>/g and to have the BET surface area of about 1400m<sup>2</sup>/g at least most preferably at least. The surface area of a particle carbon precursor influences the surface area of composite electrode catalyst powder greatly, therefore influences the electrode catalytic activity of complex powder greatly.

[0113]

Particle carbon is small enough so that it may distribute and suspend in the globule generated from the liquid precursor. As for particle carbon, according to 1 operation gestalt, it is desirable to have more preferably about 100 nanometers of mean particle diameter of about 20 to about 60 nanometers from about 10. However, the carbon particle which has the particle size of about 25 micrometers by the highest can also be used. Carbon can be made into a crystal (graphite), amorphous one, or different combination of the type of carbon. Moreover, a particle can also have the nucleus of the graphite which has an amorphous front face, or the amorphous nucleus which has the front face of graphite.

[0114]

The property of the front face of the primary particle which forms secondary support structure can be changed. The front face before the processing which forms the last particle can distribute a precursor particle in a precursor liquid. It is desirable that a front face has the controlled surface chemistry operation after the processing which forms the secondary structure. The front face of oxidized carbon can present the hydroxyl group which makes a front face a hydrophilic property more, a carboxyl group, an aldehyde group, and other functional groups. The returned carbon front face is finished with the hydrogen which promotes hydrophobicity. The capacity which chooses a surface chemistry operation enables it to adjust surface hydrophobicity, and, thereby, it becomes possible to generate an inclination to the hydrophobicity in the floor of the adhering particle. Moreover, although the carbon front face corresponding to higher surface area which oxidized tends to carry out micro etching, on the other hand, the returned carbon front face has lower surface area. An oxidation carbon front face can be used as a derivative by the reaction with various drugs which make it possible to combine various radicals containing oxygen with a front face, in order to adjust surface chemical action further. Thereby, it becomes possible to add the compound of inorganic, organic, metal organic, or an organic metal to a front face.

[0115]

In the simple source of supply of distributed carbon, the lubricant which is the suspension of the detailed carbon particle of an aqueous medium and which uses carbon as the base, such as distributed carbon black, is marketed. Especially the acetylene carbon black that has whenever [ high chemical-pure ], and good electric conductivity is desirable. The example of such carbon suspension marketed is GRAFO1322 (Fuchs lubricant company (Fuchs Lubricant, Co.) [the U.S. Illinois Harvey (Harvey) whereabouts]). This is VULCAN (trademark) which has the mean particle diameter of about 30 nanometers, and the surface area of about 254m<sup>2</sup>/g. It is the suspension of XC-72 carbon black (KABOTTO (Cabot Corp.) [the U.S. Georgia alpha RETA (Alpharetta) whereabouts]). Moreover, BLACKPEARLS (trademark)2000 (KABOTTO (Cabot Corp.) [the U.S. Georgia alpha RETA (Alpharetta) whereabouts]) and KETJENBLACK (trademark) (Akzo novel company (Akzo Nobel, Ltd.) [the Netherlands Amersfoort (Amersfoort) whereabouts]) are also desirable. This each contains the carbon which has the specific surface area of about 1300 to 1500m<sup>2</sup>/g. Other desirable classes of a carbon ingredient are activated carbon which has a certain amount of catalytic activity. NORIT which has about 20-micrometer mean diameter and the surface area of about 820m<sup>2</sup>/g for an example There are NK (KABOTTO (Cabot Corp.) [the U.S. Georgia alpha RETA (Alpharetta) whereabouts]) and PWX (Calgon carbon company (Calgon Carbon Corp.) [the U.S. Pennsylvania Pittsburgh (Pittsburgh) whereabouts]).

[0116]

A precursor can be formed in aerosol by some approaches for spraying processing, as argued above. It should not be so highly that the opposite effect is exerted on solid-state support (loading) of the carbon of a precursor solution, and aerosol generation.

[0117]

Stable precursor suspension (carbon distribution and metal salt) is required in order to guarantee homogeneous

feed. During processing, an unstable precursor precipitates to a supply reservoir, serves as a globule to which a presentation is changed, and, finally affects the property of catalyst powder. In this case, the desirable mode of operation is agitated so that a particle may not precipitate [ the suspension of the carbon particle which has the molecule precursor of a metal, a metallic oxide, or other catalytic activity matter ].

[0118]

For example, it is desirable by using a blade grinder or the high-speed blade mill of other types to dissociate bigger floc than that of carbon powder mechanically. Therefore, the thing made for water to distribute carbon powder 1) when not already provided for suspension, by mixing the desiccation powder of the amount of limitation with a wetting agent and a flexible surfactant In;3 supersonic-wave bus which dilutes the deep suspension of the time of;2 which carries out humidity of the carbon black powder with the basic surface active agent diluted by remaining water and water, secondary floc is destroyed by SONIFIKESHON of liquid suspension.

[0119]

The potassium permanganate (potassium permanganate) of the precursor of the active species of a metal or a metallic oxide dissolving in water separately, before destroying secondary floc, and adding a suitable amount to carbon suspension etc. is desirable. As for adding a metal salt by this method, it is advantageous to make it easy to destroy bigger floc, and a viscous smaller slurry is obtained by mixing. The slurry is stable for several months after SONIFIKESHON, without causing clear sedimentation or separation of a component.

[0120]

The reactor system mentioned above is not usually used for spraying processing to which the precursor of a matter component dries and reacts at one process. The particle of NANOMETORU particle size is difficult to generate, when other particles exist, maintaining control of distribution on a carrier surface. According to this invention, it is possible to change a precursor in a spray drier or a similar device, but the reason is that it uses the precursor and additive which are not more expensive than about 400 degrees C, which are desirable and are not more expensive than about 300 degrees C and which are disassembled at the temperature which is further more desirable and is not higher than about 250 degrees C.

[0121]

Carboxylate, a hydroxide, a halogenide, a nitrate, a metal organic complex, an amine adduct, an isonitrile compound, a Schiff base complex, beta diketone, alkyl, a phosphine complex, a metale phosphite complex, and metale carbonyl complexes, such as nickel, Ag, Pd, Pt, Rh, Sn, Cu, Au, Co, Ir, Ru, and Os, are contained in a useful low-temperature decomposition precursor with such low reaction temperature by this invention which forms a metal.

[0122]

As opposed to a metallic oxide to a useful low-temperature precursor Sc, Y, La, a lanthanide, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, And the oxo-complex of Sn, an alkoxide, an amide, carboxylate, There are a hydroxide, a halogenide, a nitrate, a metal organic complex, an amine adduct, an isonitrile compound, a Schiff base complex, beta diketone, alkyl, a phosphine complex, a phosphite complex, and a carbonyl complex.

[0123]

When a metal is an active species phase, it is advantageous that the additive which guarantees the reduction to the metal in low temperature can be used. Generally, this additive is a reducing agent of fusibility and can return the complex which dissolved before spraying or during spraying. As for a reducing agent, it is desirable not to return a precursor substantially at a room temperature, but to return at an about 100 degrees C - 400 degrees C elevated temperature. Moreover, these reducing agents should be stable in water, and all the volatile chemical species formed from reduction are removed from the system. an example -- borane and a borane adduct (for example, trimethylamine borane --)  $\text{BH}_3\text{NMe}_3$  and  $\text{SiH}(4-x)\text{R}_x$  (an R= organic radical and aryl --) Alkyl, alkyl with a functional group or an aryl group, a polyether, silane derivatives, such as alkyl carboxylate,  $\text{NaBH}_4$ ,  $\text{NH}_4\text{BH}_4$ , and  $\text{MBH}(3-x)\text{R}_x$  (an R= organic radical --) BORO hydrides, such as aryl, alkyl, alkyl with a functional group or an alkyl group, a polyether, and alkyl carboxylate, are contained. There is Alan (alanes) or tin hydride in other reducing agents.

[0124]

According to the desirable operation gestalt, the reducing agent of a platinum metal is especially chosen from

the group who consists of primary alcohol (a methanol, ethanol, etc.), secondary alcohol (isopropanol etc.), tertiary alcohol (butanol etc.), a formic acid, formaldehyde, a hydrazine, and a hydrazine salt. For example, at a room temperature, although the acidic solution of  $\text{H}_2\text{Pt}(\text{OH})_6$  with which a formic acid exists is stable, it is returned to Pt metal with low reaction temperature, such as about 100 etc. degrees C.

[0125]

The additive which guarantees oxidizing to a metallic oxide at low temperature can also be used for the metallic oxide as an active species phase, generally, it is the oxidizer of fusibility and this can be oxidized in the complex which dissolved before spraying or during spraying. An oxidizer is an about 100 degrees C - 400 degrees C elevated temperature rather than oxidizes a precursor to a metallic oxide at a room temperature, and returning is desirable. These chemical species are also stable in water, and volatile chemical species removable from a system should be formed. There are oxidization organic acids, such as an oxidization mineral-acids [, such as amine oxide, such as trimethylamine nitrogen oxides ( $\text{Me}_3\text{NO}$ ), a nitric acid a sulfuric acid and an aqua regia, ], carboxylic-acid, phosphinic acid ghost, hydrogen-peroxide, ozone, or sulfur style ghost, in an example.

[0126]

A precursor solution can contain other additives, such as a surfactant, a wetting agent, and pH regulator. However, it is desirable to suppress use of such an additive to the minimum, maintaining distribution of a precursor well. Catalytic activity may be reduced, when a superfluous surfactant, especially the surfactant of the amount of macromolecules remain on the front face of an electrode catalyst particle and it is not removed completely.

[0127]

Although spraying processing or a spraying pyrolysis is a useful art, the reason is that a particle is heated to an elevated temperature for a short time. Although changing a molecule precursor into a final desirable phase by being an elevated temperature comparatively is attained, since it is a short time, it is guaranteed that there is almost no diffusion of the front face which may produce condensation of the activity phase of NANOMETORU particle size. Therefore, a support phase is formed by the particle of the activity phase of the NANOMETORU particle size distributed well.

[0128]

In many application, a fuel cell or a cell is combined with other matter which is some devices, and electrode catalyst powder and other powder are often formed in a layer. The approach of adhering these matter has big effect on the property of an adhesion layer. Next, the property of an adhesion layer also has big effect on the engine performance of a device. There are control to the inclination of the presentation in average thickness, voidage, the uniformity of a presentation, the property of an interface with other phases, and a layer, hydrophobicity and a hydrophilic property, a wettability, and surface area that can be reached in the property of an important layer.

[0129]

The electrode catalyst powder of this invention can adhere on the front face of a device, or a substrate by the adhesion approach that some including direct adhesion of desiccation powder, such as dusting, electrophotography deposition, or electrostatic deposition, differ. There are the approach of liquid vehicles, such as ink jet printing, syringe measuring distribution, toner adhesion, slurry adhesion, and the paste base and electrophoresis in other adhesion approaches. In all these adhesion approaches, the powder by this invention has some advantages to the powder generated by other approaches. For example, as compared with the powder generated by the alternate method, it distributes to a liquid vehicle more easily, and the particle with small and spherical narrow distribution of particle size has carried out [ longer ] period distribution, and makes it possible to print the smoother and more detailed description.

[0130]

The electrode catalyst powder by this invention has the mol follow G and the fine structure which make it possible to form in a layer by the approach which is not useful with the electrode catalyst powder which presents high catalytic activity and has a different property. Although high catalytic activity enables a film to adhere from that of these matter, the reason is because the mass of the returned electrode catalyst is required in order to attain the engine performance of the same level. However, it is important that the advantage of powdered engine performance, such as attainment to the opening of each particle, is maintained in a layer in the process which prints a layer, for example.



[0131]

One method to which the powder of this invention is made to adhere is applying powder to a substrate by using thick film paste. In a thick-film process, the viscous paste containing a functional particle phase (for example, carbon complex powder) is screen-stenciled on a substrate. The porosity screen manufactured from stainless steel, polyester, nylon, or the same inactive substance is extended, and, more specifically, is attached in a hard frame. A predetermined pattern is formed on a screen corresponding to the pattern to print. For example, UV susceptibility emulsion can be added to a screen and it can expose through the positive image or negative image of a design pattern. Subsequently, a screen is developed and the part of the emulsion of a pattern space is removed.

[0132]

Next, it is fixed on a screen-stencil device and thick film paste deposits a screen on a screen. Subsequently, the substrate printed is arranged under a screen, and a paste passes along a screen and is extruded on a substrate by the squeegee which crosses a screen. Therefore, the locus of the paste matter and/or the pattern of a pad shift to a substrate. Subsequently, perform desiccation processing and firing processing to the substrate to which the paste was added by the predetermined pattern, it is made to solidify a paste, and a substrate is pasted up on it.

[0133]

Thick film paste has complicated chemical action, and, generally contains a functional phase, a binder phase, and an organic vehicle phase. A functional phase contains the electrode catalyst powder of this invention. A binder phase can be used as carbon, a metallic oxide, or the mixture of glass frit powder. The glass which uses PbO as the base is usually used as a binder. The function of a binder phase is controlling membranous sintering, and helping to paste up a functional phase on a substrate, and/or helping sintering of the stratum functionale. A reaction compound can also be included in a paste, in order to promote pasting up a functional phase on a substrate.

[0134]

Moreover, thick film paste also contains the organic vehicle phase whose main functions are providing a paste with a suitable fluidity (property of flow) and which are a solvent, a polymer, resin, and the mixture of other organic substance. When a liquid solvent helps to mix a component to a uniform paste and adds a paste to a substrate, it evaporates mostly. Usually, solvents are volatile liquids, such as a methanol, ethanol, a terpeneol, butyl carbitol, butyl carbitol acetate, fatty alcohol, ester, and an acetone. Other organic vehicle compounds can contain a thickener (sometimes called an organic binder), a stabilizer, a surfactant, a wetting agent, etc. A thickener provides a paste with sufficient viscosity, and acts as a binder in a non-firing condition. There are resin, such as ethyl cellulose, polyvinyl acetate, acrylic resin, and cellulosic resin, polyester, a polyamide, etc. in the example of a thickener. A stabilizer reduces oxidation and degradation, and stabilizes viscosity, or adjusts pH of a paste. For example, triethanolamine is a general stabilizer. In the technical field of thick film paste, the wetting agent and the surfactant are known well and can contain triethanolamine and phosphoric ester.

[0135]

Various components of thick film paste are mixed by the desirable ratio so that the almost uniform compound with which a functional phase is well distributed during a paste may be generated. Usually, thick film paste includes the carbon complex powder of this invention, and is about 5 - about 95 percentage-by-weight \*\*\*\*, such as about 60 to 85 percentage by weight, about a functional phase.

[0136]

The example of thick film paste is indicated by U.S. Pat. No. 4,172,733, No. 3,803,708, No. 4,140,817, and No. 3,816,097, and these all are completely used for this specification by reference.

[0137]

Some application of thick film paste needs high tolerance also for the twist which can be attained using a standard thick-film technique, as mentioned above. Consequently, some thick film paste has the optical image pick-up function (photo-imaging capability) which enables the configuration of the line and locus by which width of face and a pitch (distance between lines) are reduced. In this type of process, optical activity thick film paste is applied to a substrate, as mostly mentioned above. Polyvinyl alcohol etc. can use a paste as the liquid vehicle which is not constructing a bridge. Subsequently, it dries, and a paste is exposed by ultraviolet rays through the patternized photo mask, and carries out the polymerization of the exposure part of a paste. Subsequently, a paste is developed and the part which is not required for a paste is removed. This technique



enables it to form the line and the description of high density more. By combining the above technique with the complex powder of this invention, it becomes possible to manufacture the device which has higher resolution and tolerance as compared with the Prior art which uses the conventional powder.

[0138]

Furthermore, laser can be used instead of the ultraviolet rays which pass along a mask. Laser can scan the front-face top of a pattern and, thereby, serves as instead of [ of the need for a mask ]. The laser beam of reinforcement is fully low and does not heat the glass or the polymer above softening temperature. Subsequently, it can leave a pattern and the field where a paste is not irradiated can be removed. The conventional paste technique is the method of an and also [ it uses heating of a substrate, it removes a vehicle from a paste and it fuses a particle to one ], and makes a particle similarly embellish. Laser can be used, the layer of the paste conventionally added to the formula can be heated locally, and laser scans the paste layer top which forms a pattern. Heating of laser is limited to a paste layer, drives out a paste vehicle, and heats the powder of a paste to the forge fire which can be accepted, without heating a substrate. It enables this to heat the particle sent using the paste, without [ glass or ] damaging the substrate of a polymer further.

[0139]

According to 1 operation gestalt of this invention, it is advantageous to use direct writing type devices (the printing approach etc.), and to print the layer containing the electrode catalyst powder of this invention. The printing approach is used and there are some advantages in building energy devices, such as a cell or a fuel cell. The printing approach enables it thinly to constitute the layer which has a small characteristic particle size from a thing generable by the present manufacture approaches, such as rolling and pressing. According to a layer being more thin, mass and the volume become small, therefore the volume density and weight density of a cell become large. It can include in the vehicle which is not common, or it can unite with an electron device directly, and a thin device can be used as a compact self-warehouse actuating system.

[0140]

Moreover, more, since the diffusion length is narrow, a film can also make it easy to convey chemical species, such as ion, an electron, and gas, more quickly. Thereby for example, when that is not right, the engine performance of the cell or fuel cell whose diffusion of chemical species is a rate limiting factor can be raised. This is the case where transportation of the O<sub>2</sub> or the hydroxide ion in an air electrode is the metal-air cell which can carry out rate-limiting. With the shorter diffusion length and a lower diffusion barrier, the rate of a drain of this type of device becomes higher. A discharge rate can also be raised.

[0141]

Moreover, the printing approach can make [ rather than ] good control easy to the interface which produces the mol follow G of the inclination where the presentation was adjusted and layer front face which make chemistry transportation and electrochemical reaction easy, and construction of a layer presentation.

[0142]

A certain kind of the printing approach makes it easy to build the description which has the combined function so that it may be possible to combine with the monolayer which has two or more functions to offer an advantage for two or more layers about both the engine performance and energy density.

[0143]

Therefore, as for an electrode catalyst particle and other particles, such as a polymer qualification particle, according to this invention, it is advantageous that it can be made to adhere using a direct writing tool. In order to make it adhere using a direct writing tool, a particle must be conveyed in a liquid vehicle. The cartridge or reservoir with which the particle should often be distributed to the time amount and the liquid vehicle which were expanded, therefore suspension is arranged inside will have long storage stability. The particle of high density can be made to distribute and suspend appropriately nearly completely in some case. However, the liquid which has sufficient low viscosity for making it adhere using a direct writing tool, especially an ink jet device cannot be made to suspend the particle which has the particle size which has a high consistency as compared with the liquid which the particle is distributing according to the consistency of a particle compound, and exceeds about 0.5 micrometers. Therefore, in almost all cases, the apparent density of a particle must fully be smaller than a theoretical consistency.

[0144]

In suspension, the thing of a particle for which the buoyancy of non-<sup>\*\*</sup> is maintained mostly is desirable,

maintaining a more concrete comparatively big physical particle size. Buoyancy is required because of the stability of ink, and, on the other hand, the property of ink, such as the viscosity of useful within the limits, is maintained according to particle size being more large. That is, although settling velocity is slow, as for the particle size of a particle, it is desirable to offer a particle large enough. The settling velocity of a particle is proportional to what lengthened the consistency ( $\rho_L$ ) of a liquid from the apparent density ( $\rho_S$ ) of a particle. As for a very fine particle, it is ideal to have apparent density almost equal to the consistency of a liquid which is usually about 1 g/cm<sup>3</sup> (namely, consistency of water). Since compounds, such as an oxide, have the theoretical density ( $\rho_P$ ) of the range of about 3 to about 7 g/cm<sup>3</sup>, it is [ the apparent density of such a particle ] desirable that it is the rate that theoretical density is small. According to 1 operation gestalt, a particle has the apparent density which is not larger than about 50% as for the theoretical density of a particle and which is more desirable and is not larger than about 20% as for theoretical density. Such a particle has small apparent density, when measured by the precipitate technique, but when measured by the optical technique, it has a bigger particle size.

[0145]

In the case of electrode catalyst powder, especially the electrode catalyst powder which uses carbon as the base, it is designed so that it may have high voidage, therefore comparatively low coefficient of viscosity. This has low viscosity in these powder, and helps to make the high ink of support nature suspend powder.

[0146]

Some electrode catalyst formation may consist of matter of high density comparatively. One desirable method of gaining the apparent density with which the very fine particle by this invention was reduced is generating the particle which has the microstructure (or the combination) of hollow or porosity. A hollow electrode catalyst particle may contain the matter which uses carbon, a metal, or a metallic oxide as the base, and since it is desirable to maintain comparatively low apparent density as for the surface area of these matter, it is high. That is, the mol follow G of one desirable particle is a particle which consists of husks of the high density which has an inradius and a circumradius. Husks have high density and it is desirable that it is impermeability mostly. When it assumes that air fills the inside of such an empty capsid, the formula showing the conditions over non-\*\*\*\*\* is as follows.

[Equation 1]

$$r_2 = \left[ \sqrt[3]{\frac{\rho_p}{\rho_p - 1}} \right] r_1$$

It is an upper type and is an  $r_2$ = circumradius.  $r_1$ = bore  $\rho_L=1$  (water)

It is the theoretical density of a  $\rho_P$ = particle.

For example, when an empty capsid has the consistency of a 2-micrometer circumradius (diameter of 4 micrometers), and 5 g/cm<sup>3</sup>, the average of the optimal thickness of a wall is about 0.15 micrometers, as a particle floats at non-\*\* into the liquid which has the consistency of 1 g/cm<sup>3</sup>. According to one desirable operation gestalt, an empty capsid has the thickness of the average wall which does not exceed about 10% of the diameter of a particle and which does not exceed about 5% of the diameter of a particle more preferably.

[0147]

Please understand that other particle mol follow G can be used within desirable limits, maintaining apparent density. For example, an electrode catalyst particle can have sufficient quantity of voidage so that the particle which has apparent density smaller than theoretical density may be obtained. With the surface tension of a liquefied medium, open (front face) voidage can also make apparent density small, when a liquid is not able to permeate surface pore.

[0148]

Therefore, the very fine particle by this invention has a late settling velocity in a liquefied medium. The settling velocity by Stokes' law is defined like a degree type.

[Equation 2]

$$V = \frac{D_s^2 (\rho_s - \rho_l) g}{18\eta}$$

D<sub>s</sub>= stokes diameter Viscosity of  $\eta$ = fluid Apparent density of a  $\rho$ = particle Consistency of a  $\rho$ = liquid  
 V= settling velocity Acceleration by  $g$ = gravity The late enough thing of the average settling velocity of a particle is desirable so that it may have useful storage stability, without suspension needing to mix frequently. Therefore, about 50 percentage by weight of the rate that the mass of a particle is big having become muddy into the liquid etc. is desirable at least. As for a particle, it is desirable to have the average settling velocity which does not exceed 50% of the theoretical high fine particle child of the same presentation and which does not exceed 20% more preferably. Furthermore, after precipitate, by mixing etc., a particle can make it able to re-distribute completely and can offer distribution of the same particle size as what was measured before precipitate in suspension.

[0149]

With 1 operation gestalt, when such an additive does not have a bad influence for the compound of a hydrophilic property at the property of the electrode catalyst of a particle, an electrode catalyst particle can contain a silica (SiO<sub>2</sub>), hydrophilic carbon, other metallic oxides, or a surface treatment agent / surface active agent, in order to raise the distributed property of the powder in a liquid. The thing of the front face of a particle for which a hydrophilic compound is found on a part at least is desirable. As argued more in the detail above, as for the powder by this invention, it is usually desirable to use a spraying conversion technique and to be generated under existence of a steam. When a steam exists during formation of a particle, it is advantageous that the hydroxylated particle front face can be obtained. Such a hydroxylated front face offers the further hydrophilic property of a particle, and helps distribution of a particle, and the number of the flocs of the particle in liquid suspension is reduced.

[0150]

According to this invention, a liquid vehicle single for adhesion can be made to distribute the particle of two or more types with a direct writing tool. A liquid vehicle can be made to distribute a particle mixing lightly or by using a supersonic wave. In order to use it for an ink jet device, as for the viscosity of suspension, it is desirable that it is not larger than about 30 centipoises, and it is more more desirable than about 20 centipoises that it is not large. Moreover, it is important to control surface \*\*\*\* of liquid suspension, and, as for surface tension, it is desirable that they are about 20 to 25 dynes/cm in an ink jet device.

[0151]

As for solid-state support of the very fine particle in suspension, it is desirable that it is high as much as possible, without exerting the opposite effect on the viscosity of a direct writing presentation or other required properties. For example, as for a direct writing presentation, about 10 to about 50 percentage by weight etc. can have the amount of particle support of about 75 percentage by weight by the highest.

[0152]

Although a direct writing presentation usually uses water as the base, it is also possible to use other solvents or liquids. Although such a presentation contains a surfactant, a dispersant, a defoaming agent, a chelating agent, a wetting agent, etc., it can contain other chemicals which are not limited to this.

[0153]

More specifically, generally, an ink jet presentation contains water and alcohol. The system which uses an organic solvent as the base can also be used, and the ink jet print head is often adjusted to an organic system or an aqueous system. A surfactant is also used in order to maintain a particle to suspension. Ink becomes a lump, and the auxiliary solvent known also as a wetting agent is used in order to prevent blocking the orifice of an ink jet head. It can be used in order that an insecticide may also prevent growth of the bacteria accompanying the passage of time. The example of such an ink jet liquid vehicle presentation U.S. Pat. No. 5,853,470; by Martin and others (Martin et al.) -- U.S. Pat. No. 5,679,724; by SAKURI punt and others (Sacripante et al.) -- Carlsson et al. () [ Carlson ] et U.S. Pat. No. 5,725,647; by al. -- U.S. Pat. No. 4,877,451; by Winnik and others (Winnik et al.) -- U.S. Pat. No. 5,837,045; by Johnson and others (Johnson et al.) -- And it is indicated by U.S. Pat. No. 5,837,041 by beans (Bean et al.). Each of the above U.S. patent is completely used for this specification by reference. Selection of such an additive is based on the property known by this contractor that a presentation is

desirable. A very fine particle uses for example, a mill or an ultrasonic processor, and is mixed with a liquid vehicle.

[0154]

According to 1 operation gestalt of this invention, the liquid vehicle with which a particle is distributed to inside contains molecule precursors of fusibility, such as a metal precursor which has comparatively low decomposition temperature. Coadhesion of the molecule precursor can be carried out to powder, and, subsequently it is desirable that it is the inorganic compound of fusibility which fills all the gap space between particles and which can be heat-treated so that a continuous phase may essentially be formed. What was described on these specifications about spray drying can use a low-temperature decomposition precursor. The desirable precursor compound of a type is an alpha hydroxy carboxylate (glycolate) derivative. Metal carboxylate is often advantageous about this point about formation of metallic compounds. A molecule precursor should understand having a presentation peculiar to the adhering matter. The ligand on a molecule precursor can act as a surfactant of an actual liquid vehicle.

[0155]

With 1 operation gestalt, a molecule precursor forms the same compound as a particle and an essential target. It is advantageous that the particle of a liquid vehicle can exert a catalysis on a molecule precursor with this operation gestalt, and a desirable compound can be formed. By adding the precursor which has decomposition temperature lower than about 300 degrees C, it becomes possible to form the description of a functional group on the polymer substrate containing a polyamide, fluoropolymers, an epoxy lamination, and other substrates. These molecule precursors are useful especially when combined with the particle of hollow or porosity, but the reason is because it contributes to a higher consistency, when an adhesion layer is sintered. That is, a part of final layer originates in a particle and some molecule precursors, some precursors fill the space between particles and, thereby, it increases the solid-state part of the last structure.

[0156]

Moreover, a liquid vehicle can also contain the carrier which maintains a particle collectively, after a particle adheres. Such a liquid vehicle is advantageous, when not being sintered so that a particle may adhere and a particle may paste up mutually. Moreover, a liquid vehicle can also contain after adhesion the polymer which brings about the polymer layer which the particle is distributing in a polymer. Furthermore, a liquid vehicle can also contain a particulate material and the molecular species which can react so that the property of a particle may be changed.

[0157]

The direct writing deposition approach by this invention is roughly shown in drawing 5. In drawing 5 (a), the detailed powder 1002 is distributed to the organic vehicle 1004 containing the water which helps distribution of the detailed powder 1002, and various organic substance. The direct writing tool 1006 discharges suspension on a substrate 1008 through an orifice. The liquid vehicle 1004 which heat-treats a substrate 1008 and contains 1010 and the organic substance is removed after adhesion, and the film of a very fine particle 1002 is made to adhere.

[0158]

With the operation gestalt shown in drawing 5 (b), the particle 1012 is distributed to the liquid vehicle 1014 containing water, the organic substance and a compound, or at least one metaled molecule precursor. The direct writing tool 1016 is used for the liquid suspension containing a particle 1012, and the liquid vehicle 1014 containing a precursor, and it adheres to them on a substrate 1018. After adhesion, a substrate 1018 is heat-treated, 1020 and a liquid are removed, and a precursor is changed into each compound or metal. The layer 1022 obtained as a result contains the particle distributed through the film of a compound or a metal.

[0159]

As it is used on these specifications, a direct writing tool is a device which makes a liquid or liquid suspension adhere on a front face by discharging a liquid towards a front face through an orifice, without contacting a tool on a front face substantially. It is desirable that a direct writing tool is controllable on a x-y grid to a printing front face (that is, it is possible to move either a substrate or a device and both). One desirable direct writing tool by this invention is an ink jet device. a micro pen (a trademark --) available from an ohm craft company (Ohmcraft Inc.) [the U.S. New York State Honeoye Falls whereabouts] for other examples of a direct writing tool At automatic syringes, such as a MICROPEN tool, and a maximum of 10,000 rates/o'clock The line smaller

than it to 200 micrometers, a point, And the dot liner which can distribute a field (there is a DOTLINER (trade name) distributed system (MANKOPU (Manncorp) [the U.S. Pennsylvania alder tendon ballet (Huntingdon Valley) whereabouts]).)

[0160]

According to this invention, the diameter of the orifice of a direct writing tool can be shortened. This is as a result of [ direct ] the property of the particle about which it argued by the above of this specification. By shortening a diameter, it becomes possible to form the more detailed description.

[0161]

One desirable direct writing tool by this invention is an ink jet device. An ink jet device operates by generating the globule of ink and turning the globule to a front face. Ink jet printing is a means to send the amount which the compound controlled to various substrates, when it applies to the particle suspension by this invention.

[0162]

The location of an ink jet head is controlled carefully, and can be automated to altitude so that the discrete pattern of ink can be added to a front face. It is 1000 drops per second, or a rate beyond it, and an ink jet printer can be printed, it is about 1000cm/second in good resolution in 10cm/[ a second and ] or more than it, and the highest, and can print the linear description. Each drop generated by the ink jet head contains the liquid of an about 2 to 200pico liter sent to a front face. It is a means desirable to the altitude to which an ink jet device makes the matter adhere on a front face for these and other reasons.

[0163]

Usually, an ink jet device contains the ink jet head equipped with one or more philharmonics a cage who have diameters smaller than about 100 micrometers, such as about 50 micrometers to 75 etc. micrometers. The globule of ink is generated and it is turned to the front face currently printed through an orifice. Although a piezo-electric drive system is used and a globule is generated, as for an ink jet printer, other deformation gestalten are usually used. The ink jet device is indicated by the detail by U.S. Pat. No. 4,627,875 by KOBAYASHI and others (Kobayashi et al.), and U.S. Pat. No. 5,329,293 by Leica (Liker), and each is completely included in this specification by reference. However, such a device has mainly been used in order to make the ink of soluble dye adhere.

[0164]

As for the globule generated by the printer head, it is ideal that it is the same as that of the presentation of a bulk fluid. However, when a particle is too large to pass a channel or a loading filter, filtering suspension to some extent may be performed. The particle size of the particle of particle floc is small, and this invention enables it for the amount of the particle collected with the filter by reducing the number of particle flocs to decrease, and to remove a filter.

[0165]

According to this invention, it is possible to make the inclined layer of the matter from which the presentation of a layer changes with the thickness of a layer adhere. In order to make such a layer adhere, it is desirable that use two or more direct writing deposition processes, and the presentation of adhering suspension forms the layer which changes through a layer.

[0166]

It is also possible to use the direct writing approach of this invention, and to form the description on the front face which is not a flat surface when required for specific application or the geometry of a product, and to create the component of a device.

[0167]

A laser imprint and optical deposition are included in other processes which can be used in order to manufacture the device of this invention. By the approach of a laser imprint, the matter to which it adheres is arranged on migration substrates, such as a ribbon which uses a glass disk or an organic polymer as the base. Subsequently, a migration substrate is arranged on the substrate with which the matter adheres upwards. Subsequently, laser is used for the matter, and it is controlled and transported to a substrate from a migration substrate.

[0168]

By controlling the location of an optical fiber to a substrate, induction optical deposition is a technique which controls and sends the precursor of the matter or the matter on a substrate through an optical fiber so that the description can be formed on a substrate. the matter -- and -- or the matter is heated, when the precursor of the

matter is sent to a substrate and it is required to make the property of the matter embellish to change the matter or when that is not right. For example, the matter can be locally heated by using laser.

[0169]

Moreover, a particle is electrophoresis or can also be made to adhere electrostatic. The substrate front face which has the partial part which the particle was charged and was charged on the contrary is contacted. Lacquer processing of the layer is usually carried out so that a particle may be pasted up on a substrate. A shadow mask can be used and a desirable pattern can be generated on a substrate front face.

[0170]

Moreover, a pattern can also be formed by using an ink jet or a small syringe so that the adhesion matter may be arranged a measured part on the front face of a certain pattern. Subsequently, powder is transported to an adhesion field. Some methods can perform this migration. The sheet covered with powder can be added to the front face which has an adhesion pattern. Powder fixes to an adhesion pattern and does not fix to the surface remainder. A nozzle can be used and powder can be transported to a direct adhesion field.

[0171]

many methods of making the matter adhere directly on a front face -- a particle -- one -- sintering -- a layer -- quantity -- in order to make it dense, after adhering, it is necessary to heat a particle High dense-ization can be helped by including the precursor of the matter in the liquid containing a particle. An ink jet, a micro pen, and other liquid measuring distribution approaches can be used for the mixture of a particle / molecule precursor, and can carry out direct writing on a front face. Heating which uses partial energy sources, such as heating in a furnace or laser, may follow this. A molecule precursor is changed into the organic-functions matter contained in the particle by heating, and, thereby, fills with it the space between the particles which have the organic-functions matter.

[0172]

It is possible to use some of other approaches and to build the layer containing the electrode catalyst powder by this invention. For example, powder can be made to adhere by the approach of doctor blading, a slot die, or curtain coater. By these approaches, the ink or the paste containing electrode catalyst powder uses the blade currently maintained by specific height from the substrate, and is added to a front face. The thickness of a layer is controllable to the thickness of several micrometers at the lowest. By the approach of a slot die and curtain coater, the measuring distribution of ink or the paste are carried out through a small gap on the substrate which can be moved on the Webb drive.

[0173]

Moreover, the roll pressing approach can also be used. Mixing the component containing electrode catalyst powder, a binder, and other property modifiers, supplying them through a roll mill, and forming the compression film is included in the roll pressing approach. Roll pressing is often performed immediately on other activity sections of energy devices, such as a nickel mesh-currents collector.

[0174]

The electrostatic printing approach can be used. In this case, an electrode catalyst particle is charged with a charge, is transported to the drum of a roller, and is transported to the substrate which subsequently has a charge opposite to the charge of a particle. This migration is crossed to the whole substrate, is the method which brings about a blanket layer, or can be carried out by being the method patternized by the pattern determined according to distribution of the charge on a substrate front face. Usually, this approach enables it to transport the layer of the thickness of one particle, therefore the very good control to the thickness of a layer is attained about a film.

[0175]

The printing approach of gravure, rotogravure, and an intaglio can be used. In this case, the ink or the paste containing electrode catalyst powder is transported to the surface description of deciding the pattern transported to a substrate front face and of having often become depressed on the cylinder. A substrate is often a continuous feed stock from the Webb drive. The approach of Toppan Printing and flexographic printing can also be used. These are opposite to gravure at the point that the matter which is often in the gestalt of a paste or ink is transported to a substrate from the upheaval pattern on the front face which is often a roller.

[0176]

Moreover, the lithography approach can also be used. By the lithography approach, photosensitive ink or a photosensitive paste is arranged on a substrate, and the source of lighting or the source of electromagnetic



radiation which is generally UV light is exposed, and the exposed field interacts with this radiation and changes. It is possible to create fusibility or the insoluble description by change according to the reactivity of a paste and the liking to the lithography method of a positive or a negative. After removing the matter which is not desirable, the patterned layer included in the end of electrode catalyst powder remains for the further processing.

[0177]

The laser imprint approach can be used. In this case, it distributes on a tape or a ribbon, and laser is used for the matter including an electrode catalyst, and it transports the matter to the front face of the desirable substrate close to a tape from the inferior surface of tongue of a ribbon or a tape. The description which uses this approach and has the controlled dimension can be built.

[0178]

Moreover, the spraying adhesion approach can also be used. By the spraying adhesion approach, the ink containing electrode catalyst powder is supplied through the nozzle of spraying, and it is atomized so that the globule turned to the front face to which an electrode catalyst bed adheres may be formed.

[0179]

Therefore, when it adheres by the adhesion approach which uses such a liquid or desiccation powder as the base with the electrode catalyst powder generated by this invention, a thinner and smooth powder layer is obtained. A smoother powder layer is as compared with the powder generated by other approaches as a result of distribution of a smaller mean diameter, spherical particle mol follow G, and a narrower particle size.

[0180]

Moreover, the device containing a thin film primary cell and a thin film rechargeable battery is also made into an object, and this invention is aimed at thin film air KASOKEDO used by such cell for it with 1 operation gestalt. Thin film air cathode is especially useful in metal-air cells, such as Zn / air primary cell, and Zn / air rechargeable battery, and the new cell called metal hydride / air (MH/air) rechargeable battery on these specifications. New air cathode enables transportation to the liquid solid-state interface of O<sub>2</sub> under the reduction to the hydroxide ion (OH<sup>-</sup>) of oxygen (O<sub>2</sub>) under discharge, the transportation to the anode plate of OH-ion, and discharge. For this reason, although the thin film air cathode of 2 yuan of this invention is also called a functional oxygen electrode, that reason is that it combines both functions, i.e., reduction of oxygen and generating of oxygen.

[0181]

A metal-air cell has the optimal possibility in all cell techniques about power density, a peaking capacity property, volatile effectiveness, and rate capacity. Furthermore, the component of a metal-air cell fits very much printing which generates a lightweight and thin cell. It is advantageous to the pocket device for which high-speed discharge also needs the frequent high current discharge which has the background of low current continuous action.

[0182]

The metal-air cell by this invention has two or more stratum functionale, and the two or more can be combined with a single multifunctional layer. A membrane layer, a current collector, a non-dense water layer, an electrode catalyst bed, an electrolyte, a separator, and an anode plate can be included in the stratum functionale.

[0183]

The main electrode catalyst processes in the air cathode of other devices, such as a metal / air cell, and a PEM fuel cell, are performed on the boundary (an electrode / air / electrolyte) of a three phase circuit. This is shown in drawing 6 by a diagram. The electrode catalyst for oxygen reduction is in the zone of the three-phase-circuit contact 602, and must contact an electrode (current collector) 604 electrically, and an electrolyte 606 and air 608 must be carrying out diffusion contact. In order to attain this, a gaseous diffusion layer, a catalyst bed, and a current collecting system are contained in this metal air battery cathode. A gaseous diffusion layer is characterized by high gas permeability and the impermeability over a water solution. A catalyst bed consists of a porosity conductivity matrix which the electrode catalyst distributed to altitude so that distribution with the hydrophobic pore for oxygen supply and the pore of the hydrophilic property for exposure to an electrolyte may be brought about. A current collector is created from inactive metal mesh, such as a mesh of the nickel which is carrying out machine contact closely with the compression matrix of the carbon usually distributed highly, or a nickel alloy.



[0184]

It is desirable to make max expose an active-electrode catalytic site to air and an electrolyte. According to this invention, the inclination of the hydrophilic property / hydrophobic property which crosses the catalyst bed of a three-phase-circuit contact zone can be used, and the property of a device can be raised. Here, various operation gestalten of the air cathode by this invention are explained especially with reference to 13 from drawing 7 . It will be understood that the operation gestalt shown in 13 from drawing 7 can apply a PEM fuel cell etc. to other energy devices.

[0185]

Drawing 7 shows the air cathode 3600 by 1 operation gestalt of this invention. As for the air cathode shown in drawing 7 , it is advantageous that printing of the current collector 3602 and continuation printing of the electrode catalyst bed 3606 and the carbon conductor layer 3604 can be used. The current collector 3602 is created from conductive metals, such as nickel or silver, and its silver is desirable in many application. The current collector 3602 can be made to adhere only from the metal precursor combined with the dispersed metal powder from the metal precursor. Dispersed metal powder can be used as the powder (for example, fiber) of high aspect ratios, such as a fiber which has in altitude the 2 to 10-micrometer average length which can offer good conductivity though it is porosity, by the ability considering as the particle powder of NANOMETORU particle size. a metal precursor is not more expensive than about 400 degrees C -- it is not more preferably higher than about 250 degrees C -- it is low temperature comparatively and decomposes into the metal. For example, a silver metal precursor can be chosen from silver carboxylate and silver trifluoroacetate, and can also contain a silver nano particle. When the silver nano particle is contained in the silver trifluoroacetate precursor, pyrolysis temperature can be lowered from about 350 degrees C to about 250 degrees C. Since exposure time is short when the matter receives high-speed heat annealing, or when the lasing is carried out, it may be possible to use a hotter precursor. Heat insulation layers, such as a porosity aerogel layer, can also be used as a heat insulator, in order to reduce a thermal effect. A current collector thinner than about 1 micrometer can be formed only from a metal precursor, and although it does not need to mix metal powder, on the other hand, a thing thicker than 1 micrometer usually needs to use a metal powder precursor.

[0186]

The current collector 3602 is low temperature, and on the film gaseous diffusion layer 3603, it adheres to it and it must be processed. The gaseous diffusion layer 3603 is usually manufactured from TEFLON (trademark). TEFLON (trademark) is an available tetra-full OROE chain (TFE) fluorocarbon polymer from Du Pont (duPont deNemours) [U.S. Delaware Wilmington (Wilmington) whereabouts]. Although it is used through this specification since vocabulary called TEFLON (trademark) is simple, please understand that other same fluorocarbon polymers can be used instead of TEFLON (trademark).

[0187]

As for a current collector, manufacturing using the direct writing deposition approach is desirable. As for a current collector, it is advantageous that it is equipped with two or more pieces of-like [ long picture ] which have the width of face of a desirable average that it is not longer than about 100 micrometers -- it is not longer than about 75 micrometers. It will be understood that a metal current collector can be created by other approaches including sputtering, vacuum evaporation, a photolithography method, chemical plating, electroplating, a doctor blade, screen-stencil, or electrochemistry adhesion.

[0188]

Although the gaseous diffusion layer 3603 which uses hydrophobic pore and makes possible the maximum permeability of oxygen and the impermeability to a water solution is required, the reason is that it is necessary to prevent the pore of a gaseous diffusion layer from the flooding by the electrolyte. This layer can be used as the continuous TEFLON (trademark) film or the compressed TEFLON (trademark) reforming carbon layer. For example, thickness is about 90 micrometers and the consistency of one desirable TEFLON (trademark) layer is 2.26cm<sup>3</sup>/g. An average pore particle size is about 23nm, and distribution of pore is continued for 70nm from about 0.2nm corresponding to about 10% of voidage, and the surface area of 7.3m<sup>2</sup>/g.

[0189]

In the case of TEFLON (trademark) reforming carbon (it argues below), a current collector is incorporated as a nickel mesh of the carbon which has a near metal mesh according to a gas disconnection side face. However, in the case of the current collector to which it adhered immediately on TEFLON (trademark), it is desirable [ the

front face of TEFLON (trademark) ] that reforming is carried out so that adhesion between a current collector and a TEFLON (trademark) front face may be raised. Some paths can be used and the front face of TEFLON (trademark) can be reformed. The approach usually used in order to reform a TEFLON (trademark) front face is etching a front face. It is usually used as an industrial etching agent to tetra-dirty \*\* and TEFLON (trademark). Tetra-dirty \*\* and sodium naphthalene are mixed to ethylene glycol wood ether. TFE A TEFLON molecule is the long chain of a carbon atom which the fluorine atom combined. An etching agent tears off a fluorine atom from a chain, an electronic deficit is created, and this deficit is permuted from a steam, oxygen, and hydrogen, when TEFLON (trademark) touches air. The carboxyl group formed as a result of etching, a carbonyl group, and a hydroxyl group paste up a current collector on a TEFLON (trademark) front face simply. Thus, since it is strength, in order to etch a TEFLON (trademark) front face for etching tetra-dirty \*\* and the thin TEFLON (trademark) layer in the gestalt made into the criterion, it should dilute.

[0190]

Other technique of reforming TEFLON (trademark) is carrying out sputtering of the film of the metal membrane on a TEFLON (trademark) front face. There are Au and Cu in the example of the metal which can carry out sputtering. With 1 operation gestalt, sputtering of the 40nm Au layer was carried out on TEFLON (trademark), and, thereby, it enabled Ag current collector to paste TEFLON (trademark). TEFLON (trademark) which has the layer which carried out sputtering of TEFLON (trademark) which it was measured after the property of TEFLON (trademark) reformed the front face of TEFLON (trademark), and was etched, and the Au with a thickness of 40nm held the surface area and porosity as compared with the TEFLON (trademark) front face which is not reformed.

[0191]

In order to make the conductive current collector 3602 adhere, it is often required to anneal a precursor to a conductive metal. Therefore, in order to create a thin film cell, in the further down stream processing, it may be required to anneal the TEFLON (trademark) film. Therefore, the effectiveness of heat treatment over TEFLON (trademark) was investigated. Some strips of TEFLON (trademark) were put on the furnace at different temperature for 10 minutes. since the glass transition temperature of TEFLON (trademark) is 340 degrees C as measured from TGA/DTA data -- change of the property of TEFLON (trademark) -- being certain -- \*\* -- it carried out and was measured at 100 degrees C, 200 degrees C, 250 degrees C, and 300 degrees C. When the strip which made such and was obtained was heated for 10 minutes at 300 degrees C in the furnace, the surface area of TEFLON (trademark) decreased from 7.3m<sup>2</sup>/g to 5.9m<sup>2</sup>/g. Since the reduction in surface area is directly related to reduction of diffusion of the gas which passes along this layer, it is not desirable. At temperature lower than 300 degrees C, it was changeless to surface area and porosity.

[0192]

The alternate method heated at a furnace is using quick heat treatment. Quick heat treatment (RTP) is the many-sided technique for the processing facility from which some, such as quick heat annealing (RTA), quick heat cleaning (RTC), and quick thermochemistry vacuum evaporatio (RTCVD), differ. A quick heat system can raise temperature exceeding 200 degrees C/s. A quick thermal process heats the matter to processing temperature with radiation heating.

[0193]

The strips of TEFLON (trademark) are 200 degrees C, 250 degrees C, 300 degrees C, and 347 degrees C, respectively, and annealing was carried out for 1 minute, respectively. Each of a TEFLON (trademark) strip to which RTP was given by different measurement is characterized in respect of surface area and porosity. When RTP was given to a TEFLON (trademark) strip at 347 degrees C, it was observed that surface area decreased to 5.3m<sup>2</sup>/g. However, at temperature lower than 347 degrees C, it was changeless to the surface area of TEFLON (trademark) on the occasion of quick heat treatment of a TEFLON (trademark) strip. Therefore, it is an elevated temperature and it is more possible than heating at a furnace to give RTP to TEFLON (trademark).

[0194]

With an example, it adhered to the silver current collector on the TEFLON (trademark) film etched using the direct depiction approach. Silver trifluoroacetate (trifluoroacetate) and a silver metal nano particle were contained in the silver precursor. After adhesion, the assembly was heated for 10 minutes at 250 degrees C so that a current collector might be formed. The width of face of an average of a current collector line is about 75 micrometers.

[0195]

When drawing 7 is referred to again, the electrode catalyst 3608 is an oxygen deficiency Co-nickel-O metallic oxide in a rechargeable battery, and it is desirable that they are complex MnOx/C or Pt/C in a primary cell. In order to form the electrode catalyst bed 3606, the electrode catalyst particle 3608 is distributed by the hydrophilic matrix 3610 which has hydrophobicity lower than the hydrophobic matrix 3614. The carbon conductor layer 3604 is required in order to offer conductivity between a current collector and the electrode catalyst bed 3606. The carbon particle 3612 is distributed by the hydrophobic matrix 3614 in this layer. Although it is desirable to consist of matter to which it may adhere by the direct depiction approach as for a separator 3616, screen-stencil, a doctor blade, or other technique can be used.

[0196]

The hydrophobic matrix 3614 can include fluorocarbon polymers, such as a gestalt of carbon of a certain kind, and TEFLON (trademark), and other organic chemistry kinds. A hydrophilic layer can include the carbon-electrode catalyst by which coating was carried out with the metallic-oxide activity phase for the matter which uses a metallic oxide as the base. Some types of carbon and the organic polymer of the shoes guided by the hydrophilic functional group (for example, polyester, polyethylene oxide, a polyether, polyalcohol, and poly carboxylate) can also be used. Desirable hydrophilic polymers are hydrophilic fault fluoro hydrocarbon polymers, such as NAFION (trademark).

[0197]

In order to form the carbon conductor layer 3604 and the electrode catalyst bed 3606, the carbon particle 3612 and the electrode catalyst particle 3608 are the thickness distributed and controlled in the liquid vehicle, and can be printed to a mutual top, respectively. To form a hydrophobic matrix, by coating with TEFLON (trademark), a carbon particle and/or an electrode catalyst particle can be made into the polymer by which reforming was carried out, and can control hydrophobicity adjusting the rate of TEFLON (trademark) to a particle, or by incorporating a hydrophilic polymer.

[0198]

One advantage of the operation gestalt shown in drawing 7 is that it is desirable that the whole thickness is not larger than about 100 micrometers (except for a separator 3616). Thereby, some amelioration including the diffused resistor of these layers having been reduced is brought about. The thickness of the current collector 3602 becomes thin, and besides the higher rate of a drain, the small volume is obtained rather than it corresponds to bigger volume energy density and weight energy density. Although the rate of a drain was more high, after being removed by using the catalyst matter with the limitation of movement of an electrode catalyst more effective [ the reason ], the next limit to catalyst conversion is because chemical species become the rate which can be diffused between layers. Therefore, in order that mass and the volume may decrease in this specification (a liquid electrolyte is used in contrast with a solid electrolyte), volume energy density and weight energy density not only increase, but the chemical species to diffuse run a shorter distance and shorter transportation time amount, therefore the quicker rate of a drain are obtained. Although this is the advantage of Li ion cell, it is because the chemical species (Li ion) to diffuse pass along the solid-state LiMnOx spinel electrolyte of a metallic oxide and it is still spread comparatively slowly, for example, even when the printed current collector is used for the reason.

[0199]

Drawing 8 shows the air cathode 3700 including the printed current collector 3702 and the inclination of the electrode catalyst concentration which passes along a layer 3705 by other operation gestalten of this invention. Layers 3604 and 3606 ( drawing 7 ) are combined with the single inclined layer 3705 ( drawing 8 ). The same current collector metal as what it argued about above with reference to drawing 7 can be used. As for the part to which the part which the layer of carbon and an electrode catalyst is combined with the single inclined layer 3705, and contacts the current collector 3702 contacts a separator 3716 including a hydrophobic matrix, the thickness of an electrode is remarkably reduced including a hydrophilic matrix. According to this, the rate of a hydrophobic matrix and a hydrophilic matrix changes through a layer 3705. All manufactures of the inclination in the presentation of an electrode catalyst / conductor layer 3705 need to print the continuation layer which is changed about extent of the concentration of the hydrophobicity which brings about improvement in the engine performance, and the electrode catalyst particle 3708, and the concentration of the carbon particle 3712 and which has the changing presentation (for example, TEFLON (trademark) and/or NAFION (trademark), and a

carbon particle comparatively). Therefore, the film of a different presentation can be printed continuously and the presentation of each class changes systematically. The adjusted presentation inclination is generated by this, therefore a desirable property can be attained. As an alternative, the presentation of a precursor may change continuously and a repetitive layer brings about the inclination of a presentation.

[0200]

One advantage is that the whole thickness is reduced further and higher energy density is obtained. As for a current collector and an inclined layer, it is desirable to have the thickness of an average of the whole which is not larger than about 50 micrometers. Furthermore, a bigger three-phase-circuit contact zone is created by the inclination of a presentation, and the too more good engine performance is brought about.

[0201]

Drawing 9 shows other operation gestalten containing the electrode catalyst particle layer 3808 printed immediately on the current collector 3802 of the air cathode 3800 by this invention. As for the function in which some layers were put together, it is advantageous to eliminate a carbon layer and to offer a further more thin electrode. Since the current collector 3802 and the electrode catalyst particle 3808 touch closely, the carbon which was required for conductivity ( drawing 7 and 8) is eliminated.

[0202]

Some technique can be used and the electrode catalyst 3808 can be adhered on the current collector 3802. The electrode catalyst 3808 can adhere using the direct depiction approach, or can be formed immediately on the current collector 3802 by vapor phase adhesion.

[0203]

As for the thickness (a separator 3816 is not included) of an electrode, as compared with about 400 micrometers of the conventional structure, it is desirable that it is not larger than about 30 micrometers. Therefore, a diffused resistor is reduced and the better engine performance is obtained.

[0204]

Drawing 10 shows the air cathode 3900 including the complex current collector / electrode catalyst 3903 by other operation gestalten of this invention. This structure combines the function of a current collector and an electrode catalyst with the single porosity conductivity printing pattern 3903. The oxygen which passes along a layer 3903 does not need to be spread.

[0205]

With this operation gestalt, an electrode catalyst and a current collector are combined with the porosity complex structure 3903 by the controlled humidity so that the interface of a three phase circuit may be formed. This is attained by combining the electrode catalyst particle 3908 formed beforehand and the precursor of the porosity metal which can contain metal particles and a metal precursor. A metal precursor is changed into a metal by heat treatment at low temperature, metal particles are combined, and the layer 3903 of porosity including an electrode catalyst is formed. A layer 3903 can use the ink of the silver containing electrode catalyst particles, such as NiCoOx, or nickel etc. as metal ceramic complex. In this case, a low-temperature path (for example, porosity fluorocarbon polymer) can be used rather than it coexists with a substrate. Other additives which help to disassemble a silver precursor and to form silver, such as a reducing agent, can be included. The silver paste used in the applicable field of a polymer thick film also has useful possibility.

[0206]

Furthermore, complex particles, such as a metal / metallic-oxide particle, have a useful thing in this layer. For example, a metal or metal alloys, such as Ag/Pd which has the embedded perovskite metallic oxide (for example, MgTiO<sub>3</sub>), have a useful thing.

[0207]

With this operation gestalt, the electron generated on the front face of the electrode catalyst 3098 is directly captured by the current collector 3902. Thereby more good current collector efficiency and the quicker rate of a drain are obtained.

[0208]

Drawing 11 shows the air cathode 4000 by other operation gestalten of this invention. Cathode 4000 includes a porosity complex current collector / electrode catalyst 4003. The complex layer 4003 combines a current collector and an electrode catalyst with the continuation porous layer 4003, and this continuation porous layer also contains hydrophobic modifiers, such as a fluorocarbon polymer. There are an emulsion containing Liquid

TEFLON (trademark) and a small TEFLON (trademark) particle or various fluorocarbon polymers by which reforming was carried out in an example. A TEFLON (trademark) emulsion is incorporable one of the approaches which were mentioned above. Oxygen can be diffused through the porous layer which is the thickness of about 30 micrometers.

[0209]

It depends for the technique of this complex layer on mixing some components containing a metal, TEFLON (trademark), and the particle of the electrode catalyst which has other components. Metal particles have distribution of the controlled particle size. The particle size of the pore often controlled by this is obtained, and the particle size of pore is decided with the size of the space between particles.

[0210]

The inclination of various complex of a type can be manufactured about the complex layer 4003. For example, the inclination of voidage can be formed by controlling distribution of particle size as a function of the location in a layer. A hydrophobic inclination can be formed by changing the concentration of the TEFLON (trademark) type matter. The concentration of an electrode catalyst can also be changed. Furthermore, conductivity can be changed by controlling metal particles and a molecule metal precursor.

[0211]

Steamy osmosis can also be used in order to form various useful structures which were mentioned above. In this process, the floor of a particle uses a direct depiction process and it adheres to it first. In order that a floor may be heated and may make a metal or a metallic oxide adhere, it is exposed to the reaction steam which carries out CVD or ALE. This steamy osmosis approach is the capacity to make the catalytic activity which improved, the capacity to which welding of the particle is carry out mutually, the capacity to oxidize or return a certain chemical species, the capacity which controls a reaction peculiar to a part, MnO<sub>2</sub>, silver, and other metals and metallic oxides adhere at low temperature and suitable silanizing, or the same drugs, and has some potential advantages including the capacity which reforms the hydrophobicity of the matter.

[0212]

In order to build the device of a three-dimension layer, the mutual "monolayer of a particle which forms the three-dimension AKI tee tea whose engine performance improved considerably" can be made to adhere. As a current collector which has the monolayer of an electrode catalyst particle, this technique is the most useful, when carrying out the alternation of the monolayer of metal particles. According to this three-dimensional structure, the engine performance improves as a result of high surface area, and a conductor and close contact of an electrode catalyst particle. This design is roughly shown in drawing 12.

[0213]

With the operation gestalt shown in drawing 12, a device 4100 can be manufactured as follows. The direct depiction approach is preferably used for the base 4102 (gaseous diffusion layer), and coating is carried out in the complex layer 4103. This can be carried out with two or more serial jet/heads which have a presentation which is different in each so that a semi- inclination may be formed. A layer 4103 contains the mutual film of a current collector particle (4105, 4106, 4107, 4108) and an electrode catalyst particle (4109, 4110, 4111). A particle layer is distributed by the hydrophobic matrix near the base 4102, and the hydrophilic matrix near a separator 4116. The ratio of hydrophobicity/hydrophilic property changes through the thickness of a layer 4103 according to it. Subsequently, the overcoat of an electrolyte presentation uses the same approach or other same techniques, and it is added. For example, an electrolyte is potassium-hydroxide potassium. It can consider as the water solution of hydroxide and KOH. This can be made to adhere as a part of ink formation through a printing layer, and an additional overcoat may not be required in this case. A layer can be made to adhere without needing an electrolyte, and an electrolyte can be behind added as an overcoat, in order to make the layer which is downward permeate, when it can be made to adhere using the approach of being equal to the corrosion of KOH. Subsequently, the direct depiction approach is used and the separator layer 4116 is added.

[0214]

When reducing a characteristic particle size of air cathode, and the thickness of a layer, it is expected that the point that the further reduction of particle size is harmful to the engine performance of a cell exists. It is possible to print the layer which is the thickness of about 1 particle corresponding to the dimension of about 1 to 2 micrometers. such sizes -- some parameters, such as an inclination of pH, concentration, and electric field, - the engine performance of a device -- influencing -- probably -- \*\* -- it may be harmful. The layer in which

this may have the most serious effectiveness is in a current collector. It can change to the fine porous layer which may restrict the engine performance of a cell for a big IR drop from the limit of a grid with the width of face and the pitch of a line almost "transparent." It is shown that there is no remarkable problem of an IR drop to particle size with count as characteristic at the lowest as the thickness of a 20-micrometer layer.

[0215]

One of the problems relevant to the cell which uses an electrolyte is that carbonate is formed from CO<sub>2</sub>. CO<sub>2</sub> reduction zone can be used and this problem can be mitigated. For example, the selective absorption of CO<sub>2</sub> by metallic oxides of high surface area, such as a group II metallic oxide, can be used. It is what should be taken into consideration that molar volume increases in case MO to MCO<sub>3</sub> is formed when reacting with CO<sub>2</sub>, and this will convey the mass to which O<sub>2</sub> was limited in the cell according to voidage and other factors. Therefore, although a heavy-metal oxide is desirable, the reason is that expansion of the volume decreases and the atomic weight of a metal ion increases. As an alternative, a layer can be used and the catalytic reaction which changes CO<sub>2</sub> into inactive chemical species or still more useful chemical species can be started. This can have the additional advantage that the oxygen which can become useful is formed in the engine performance of a cell. This layer must be arranged between air and an electrode catalyst bed. Drawing 13 (a) and 13 (b) show two arrangement to this layer. In drawing 13 (a), CO<sub>2</sub> reduction-zone 4218a is arranged between electrode catalyst bed 4206a and carbon conductor-layer 4204a. With the operation gestalt shown in drawing 13 (b), CO<sub>2</sub> reduction-zone 4218b is arranged between base 4201b and current collector 4202b.

[0216]

It is especially advantageous, although it is this invention and the thin film air cathode mentioned above is also used for the electrode of cells which can be charged, such as a charge type zinc air battery. A zinc air battery is roughly shown in drawing 14 (a) and 14 (b).

[0217]

Specifically, drawing 14 (a) shows the zinc air battery 500 in charge mode. A cell 500 contains the air electrodes (cathode) 502 and 508 and the zinc electrode (anode plate) 504 containing the layer of zinc 506. An electrode is usually mounted in the flat container currently opened to air. When a cell discharges, the zinc metal 506 oxidizes to Zn<sup>2+</sup>. When all zinc oxidizes, a cell 500 is charged and Zn<sup>2+</sup> is returned to the zinc metal 506. using the direct depiction deposition approach of this invention, and making metal-carbon complex powder adhere by the discrete pattern -- thin -- quantity -- it is advantageous that such an electrode catalyst device that has dense structure is generable.

[0218]

Moreover, this invention also makes an object the new cell system which is the hybrid of the existing metal hydride, and the zinc / air technique called metal hydride / air (MH/air) cell. The property of various cell systems is shown in Table 1.

[Table 1]

表 1. 電池システムの特性

電池システム	比エネルギー (Wh/kg)	エネルギー密度 (Wh/L)	比出力 (W/kg)	サイクル 寿命
Li-イオン	250	200	100-200	1000
金属水素化物	70	250	70-280	500
亜鉛/空気	250	200	200-450	200
金属水素化物 / 空気	320	250	100-350	1000

As for the metal hydride/air cell by this invention, it is advantageous to combine the advantage of the anode plate from a metal hydride cell with the air cathode of this invention. As shown in Table 1, although, as for metal hydride/air cell, specific high energy, specific power, etc. offer many of advantages of zinc/air cell, it also has the extended cycle life.

[0219]

As for the metal hydride/air cell by this invention, an alkali electrolyte is arranged between two electrodes



including a metal hydride anode plate and air cathode. Oxygen and water are changed into a hydroxide ion during discharge, this is conveyed to an anode plate, it can react with metal hydride and an electron can be formed there, and this electron can be routed so that energy may be generated. Water reacts in a metal hydride electrode during charge, a hydroxide ion is created, and subsequently, this reacts in an oxygen electrode and separates oxygen.

[0220]

The GPS (earth scale positioning system) transceiver of the metal hydride/air cell of this invention etc. is useful especially in the miniaturized device. each metal hydride / air cell cel -- the output of about 0.9 volts -- it can provide -- such [ at least ] four cels -- a GPS cell -- it is, and it is used and GPS business is provided with the electrical potential difference of 3.6 volts by the whole which comes out enough and exists. A cell is thin, is lightweight and can be charged many times. It is expected that each cel has the mass of about 4g. Although a cell has slightly low power density from a zinc air battery, a cell has far more long useful life longevity. The air cathode which makes charge possible can adjust the engine performance to various application combining various anode plates. Although a driverless car, a smart card, a GPS transceiver, RF tag, various sensors, immunoassay, the telemetry, and other pocket communication links can be included in such application, it is not limited to this.

[0221]

Drawing 15 shows the metal-air cell in discharge mode roughly. Drawing 16 shows the metal air battery in charge mode roughly. The metal-air rechargeable battery was restrained by the problem of an air electrode before. Repetition charge nature, a cycle life, and environmental stability were included in said problem.

[0222]

The direct writing deposition process of this invention enables it to manufacture the above high performance cells. An approach can be applied to a different performance requirement, a thin lightweight layer is generated, and cost effectiveness is high and uses the matter efficiently. The capacity which controls adhesion by the digital method enables it to perform an easy design change.

[0223]

As for a cell, it is advantageous to offer the improved volume energy density, a weight energy density, the capacity which increased, the extended cycle life, a higher discharge rate, and an extensive temperature requirement of operation.

[0224]

Moreover, this invention is applicable to some other cell techniques. For example, as for methodology, it is advantageous that it is applicable to creation of a prism cell. As for the methodology of this invention, it is advantageous to enable increase of the number of charge cycles, increase of power density, increase of a specific output, reduction of the thickness of a layer, and reduction of the thickness of a cel, and to bring about a thereby more small device.

[0225]

The electrode catalyst powder and other matter which can be manufactured by this invention are useful also to a fuel cell. There are a proton exchange film fuel cell (PEMFC) and a phosphoric-acid fuel cell in the example of a fuel cell. It is the reaction of a fuel -- as for the class of a fuel cell reaction with the need of doing a catalysis, hydrogen gas (H<sub>2</sub>) forms H<sup>+</sup> -- and in PEMFC, H<sup>+</sup> passes along H<sup>+</sup> ion transport film, and is conveyed to cathode. In this case, generally a fuel cell operates in an acid medium, and cathode returns O<sub>2</sub> and, finally forms water as an end product. Other fuels, such as other hydrocarbons, such as a methanol, natural gas, or methane, can be used. Other gas which may pollute reactions, such as CO, or a catalytic activity part exists in some of these cases. These gas must be removed by existence of the alternative activity presentation of the presentation which oxidizes a fuel. Consequently, an electrode catalyst helps removal of such chemical species, or conversion to a good nature product. A catalyst is also needed in order to change feed fuels, such as natural gas, into a reactant with more contents of H<sub>2</sub> in some cases. Thereby, the effectiveness of a fuel cell improves and the configuration of catalyst contamination is reduced. The catalyst presentation of this invention is also useful although a catalysis is exerted on this reaction.

[0226]

PEMFC is equipped with the output conditioner and balance of the power section of the following sections, i.e., a fuel processor, or a reformer, and a fuel cell stack, and a plant. About these components, it argues below.

[0227]

Hydrogen is abundant and, as for a fuel processor or a reformer, carbon changes natural gas or other fuels into few gas streams of a monoxide. In order for the chemical species which may pollute electrode catalysts, such as CO, to recognize low concentration existence of a presentation and engine performance of the electrode catalyst powder of PEMFC at the natural gas by which the reconstitution was carried out, it has big effect on the design of this component. When ideal, it is supplying pure hydrogen to PEMFC, and although a reformer is unnecessary in this case, it is the case in which this is impossible in the future which can be predicted since the existing hydrogen distribution infrastructure is lacked.

[0228]

Each fuel cell stack is equipped with some membrane electrode assemblies (MEA). MEA is a field where gas (a fuel and air) is sent, and conversion to electrical energy from a chemical is performed by the electrode catalyst in response to a catalysis. Each MEA generates the useful electrical potential difference of about 0.6 V, and the number of MEA(s) connected to the serial used for a stack shows the electrical potential difference of the whole system.

[0229]

MEA is roughly shown in drawing 17. Each MEA is equipped with some components. The proton exchange film (PEM) 1702 is a proton transfer electronic insulator layer alternatively conveyed to the cathode which reacts the proton formed in the anode plate with oxygen ion, and forms water and the electrical and electric equipment. PEM is a sulfonation fault fluoro hydrocarbon (sulfonated perfluorohydrocarbon), and is usually called by the trade name NAFION (trademark) on these specifications.

[0230]

An electrode mainly consists of an electrode catalyst and an activity catalyst is the platinum or the platinum group metal which is generally written to be Pt/C and which was supported on conductive support, such as carbon. Although the business to the presentation of an electrode catalyst is various, the reason is that a different reaction occurs with each electrode.

[0231]

Anode plate:  $H_2 \rightarrow 2H^{++} + 2e^-$  Cathode:  $4H^{++} + O_2 + 4e^- \rightarrow 2H_2O$  Generally the cathode electrode catalyst 1704 is Pt distributed on carbon. In the case of pure hydrogen, the anode plate catalyst 1706 is also Pt/C. Thereby, a fuel cell becomes easy and the cost also falls. However, temporary increase of CO concentration is generated and the alloy catalyst containing a ruthenium/platinum alloy (PtRu/C) is usually used on carbon for the non-dependability of the reformer which may destroy a Pt/C catalyst completely. As mentioned above, the design which is adapted for the engine performance of these matter and the engine performance of a reformer is important for the cost dependability and the engine performance of a fuel cell. The costs and the engine performance of an electrode catalyst which used these noble metals as the base are the cost of a fuel cell, and the main factor of the engine performance.

[0232]

A gaseous diffusion layer is a layer of the porosity hydrophobic matter which generally uses carbon as the base, and this is offered between the gas delivery channels and electrodes which are contained in 2 pole plate, and distributes a gas uniformly on the front face of an electrode.

[0233]

One pair of current collectors usually incorporated in 2 pole plate exist in each MEA so that the electron (namely, electrical and electric equipment) generated during the conversion to electric generating power from chemical fuel may be captured. 2 pole plate is used, and MEA is supported mechanically, and gas is uniformly distributed on the front face of gaseous diffusion, and an electrode layer.

[0234]

The balance of a plant needs the remainder of a fuel cell. All the interfaces of a module of operation, the electrical and electric equipment, and a fuel are a part of this group of a standard facility.

Electric generating power explains actuation of PEMFC to a detail further paying attention to the actuation of MEA generated from a fuel. It is important for the engine performance and dependability of the upper result of a fuel cell to understand the business of the matter system contained of operation, and the basis to a remarkable contribution of the matter of this invention and the related direct writing technique which became possible is offered. An important interaction exists between the need for the developed matter system, and the approach to

which these matter is made to adhere so that the optimal structure and the optimal function may be attained in these layers. Two or more functions which need in principle the structure of competing in many cases exist. This is the basis of this invention which enables adhesion of a highly efficient multifunctional layer according to a direct writing process.

[0235]

PEMFC Four steps shown in drawing 18 explain actuation of MEA. A fuel cell should operate continuously and should care about that it is supposed that these phases are the same here because of an understanding of a process. A cell operates by the steady state of given loading, therefore it connects and the process is balanced.

[0236]

In this case, it is assumed that hydrogen was gained from the reformer which was used as a fuel, and was supplied as a pure fuel, or is not polluted. Hydrogen is sent through 2 pole plate and distributed from the source on the field of a gaseous diffusion layer (GDL). Hydrogen is diffused through a gaseous diffusion layer until it reaches an anode plate layer. Although GDL is a gas permeability layer which has pore structure and makes it easy to distribute gas uniformly by passing the pore, it does not bring big pressure drawdown to a system. In order to prevent drying an anode plate layer, generally hydrogen gas is moist and, thereby, brings about ion convective loss. Therefore, GDL must be able to process water, without affecting gaseous diffusion capacity remarkably. Therefore, GDL is designed so that the balance of the property of hydrophobicity and a hydrophilic property which has distribution of the pore with which it is not closed by changing the level of water may be attained, and it may have the combination of the required matter.

[0237]

An anode plate (and cathode) layer must have the structure with which the following attributes are equipped, i.e., gaseous diffusion, an alternative ionic diffusion, ion convective, and alternative electronic conductivity including an electrode catalyst (for example, Pt/C), water, and the mixture of a proton transfer polymer. The role of an anode plate layer oxidizes hydrogen with a catalyst, is the minimum possible temperature, and is forming a hydrogen ion and an electron. A layer must be designed so that all catalytic activity Pt front faces can reach a hydrogen content child at the maximum effectiveness, and it may be porosity for hydrogen gas. After a proton and an electron are formed, an electron is alternatively removed through the conductive network of carbon-electrode catalyst support to a current collector (that is, an electron should not move to cathode through the proton exchange film). Therefore, a layer must not be porosity, so that a carbon particle is not connected. The proton formed in Pt catalyst passes along the remainder of an anode plate layer, and must be conveyed to the film. This ionic diffusion needs the medium which makes this kind of diffusion easy, and the business to this is nearly completely opposed to optimization of gaseous diffusion. Ion proton diffusion needs [ an aquosity proton transfer polymer etc. ] the thing with the network of the liquid or solid-state with which even the proton exchange film conveys a proton it is [ the thing ] closely in contact also for a catalytic activity part. In (it is applied also to cathode), and an electrochemistry system, this situation that described the anode plate is known well, and, generally is called a three-phase-circuit interface (refer to drawing 6 ). Construction of a three-phase-circuit interface had been a problem in the general electrochemistry system for a long time. The matter system and the adhesion approach of this invention offer the solution made possible to this problem of adjusting the structure and the function of a three-phase-circuit interface.

[0238]

A proton passes along the proton exchange film and is alternatively conveyed to cathode. This is attained by using the film which enables transportation of a proton alternatively and prevents remarkable leakage of water, although it is insulation electrically (in order to avoid electronic conduction). Operating temperature and mechanical reinforcement are contained in the problem relevant to the engine performance of PEM. Although operating a fuel cell at an elevated temperature more makes higher current density possible, the operating temperature of a fuel cell is NAFION (trademark). It is restricted by the thermal stability of PEM. In order to manufacture MEA with the large volume, it is required to use the high-speed manufacture process which will use as the base the reel two Lille Webb drive which needs PEM of high mechanical strength rather than current achievement is possible using pure NAFION (trademark).

[0239]

After being alternatively conveyed by PEM, a proton must find the path to the catalyst of cathode which can react with oxygen ion and can form water in this phase. Transportation of this ion needs a promotion medium

like the case of the ion transport business in an anode plate. On the other hand, oxygen is the business of it being spread through a gaseous diffusion layer, distributing to homogeneity, and arriving at cathode, and was supplied to cathode. However, since water is formed in this case in cathode, the source of oxygen (usually air) is supplied by dryness so that removal of the generated water may be made easy. This is attained by carrying out humidity, in case the constituent of the remaining air passes through cathode and comes out from cathode. Then [ return and ], the electron generated in the anode plate is conveyed through the work load of an external environment, and is again distributed by the current collector in cathode at catholyte. The conductive carbon particle of cathode distributes an electron to the active site of an electrode catalyst, it arrives, and it is returned and an oxygen atom forms oxygen ion ( $O_2^-$ ) there. Two protons react with each oxygen ion, and form water 1 molecule. Therefore, the diffusion of gas and ion of the design requirement of cathode is the same as that of the design requirement of an anode plate with electronic conductivity at the point of being required. Moreover, cathode must be able to correspond to formation and removal of water, without doing the opposite effect.

[0240]

GDL which has covered cathode is this phase and must be able to remove the water generated in the cathode other than sending the dry air which is the origin to which oxygen reacts alternatively in cathode. As this was also mentioned above to GDL of an anode plate, it must be attained by choosing appropriately the matter, the structure of a layer, and the adhesion approach of a layer.

[0241]

The engine performance of MEA is mainly judged on the basis of the electrical potential difference of MEA and the relation of current density which are often called a polarization curve. The example of a polarization curve is shown in drawing 19 . The easy explanation about the effect of a MEA design to the property of a polarization curve is as follows.

[0242]

A polarization curve shows the general configurations of the electrical potential difference of a cel, and the relation of current density. It is desirable to shift to a higher electrical potential difference to the given MEA engine performance (for example, specific polarization curve), when a better fuel and effectiveness of operation are required. Although the effectiveness of the cel generally becomes higher by operating PEMFC by the high voltage more, since power density becomes lower, a bigger cel is needed. Although the cost of capital which builds a cel increases by this, cost of operation becomes cheaper. Although actuation on a lower electrical potential difference generally serves as low effectiveness more to a given polarization curve, it needs a smaller cel (since power density is higher), therefore although a cost of capital becomes cheaper, cost of operation becomes higher. It is advantageous to make higher the location (vertical position) of the lengthwise direction of a polarization curve (that is, higher current density is attained on a lower electrical potential difference). A curved vertical position is greatly influenced by the quantity of the matter, and the factor including platinum support of operation. Although more platinum is more good, increasing contributes the amount of platinum to cost greatly. The presentation of temperature and gas and a gaseous usage are contained in other operational parameters, and these all affect the cost and dependability of PEMFC. The purpose which designs MEA makes max the vertical position (namely, engine performance) of a polarization curve, and, on the other hand, is holding down the cost, the cost of capital, and the cost of operation of a component of the matter to the minimum.

[0243]

The relation between the configuration of a polarization curve and the structure of MEA is understood well, and as shown in drawing 20 , it can be divided into various fields. These fields are PEMFC. It has the kinetics (kinetic) of actuation of MEA, electric resistance (ohme), and the field restricted by transportation.

[0244]

In an operating range, the engine performance is mainly shown by the reactivity of the movement engine performance, i.e., a catalyst. If a catalyst carries out activity more, the electrical potential difference of the cel in given current density will become higher. The activity of a catalyst is shown by the structure and the number of active sites.

[0245]

In an electric resistance field, the engine performance is mainly shown by transportation of ion and an electron. Therefore, the better engine performance is shown to the altitude for electric conductivity by the good relation

between a conductive carbon particle and the good network of the proton transfer polymer which connects the catalytic activity part of an electrode catalyst to PEM.

[0246]

In a transportation zone, the engine performance is mainly shown by the diffusion of gas chemical species from the active site of the active site of an electrode catalyst, or an electrode catalyst. The better engine performance is clear from the gas distribution manifold of 2 pole plate by the quick diffusion which passes along a gaseous diffusion layer and the suitable pore of gas which passes along an electrode.

[0247]

It is clear from this explanation that the matter and the structure of a layer equipped with these matter have very big effect to the engine performance and cost of a PEMFC system.

One of the main purposes of this field increases use of Pt, it is the minimum possible Pt support, and is making it have best performance. Based on supporting Pt on carbon support, and loading [ both ] the electrode layer of MEA with a carbon support electrode catalyst, the method by which some differ can attain this. As mentioned above, according to the operating condition of a fuel cell, delicate balance exists about the usage (therefore, cost) of the engine performance and Pt.

[0248]

By improvement in pure movement obtained from the usage of improved Pt, change of a maximum of 0.35 A/cm<sup>2</sup> breaks out. Therefore, when the purpose is operating a fuel cell under the conditions of current density lower than 0.35 A/cm<sup>2</sup> or an electrical potential difference higher than 0.75V, the improvement in movement is enough. However, although the effect which gives the improvement in movement to the improvement of layer structure and the matter as opposed to the actuation under different conditions with an electrical potential difference lower than 0.75V and larger current density than 0.35 A/cm<sup>2</sup> is not more remarkable, the reason is that this is the field influenced by an ohm property and transport properties. Therefore, under these conditions, the polarization curve shown in drawing 21 can be obtained by improvement of layer structure. The importance of this improvement is reinforced by the output performance diagram shown also in drawing 21.

[0249]

This background is important for understanding the approach of optimizing the usage of platinum by changing both Pt content of an electrode catalyst, the thickness of an electrode layer, and structure. This point can be explained as follows. Drawing 22 can show three layers of active substances A, B, and C, and these layers can make a gaseous diffusion layer or the ion electric conduction film the electrode catalyst bed which adhered on support. By using support of Pt to the same carbon on C, such as 20w.%Pt, the amount of weight support of Pt measured in mgPt/cm<sup>2</sup> of B will double A, and C will be 3 times the amount of support of A. Although it may be very similar to the thing (that is, it can set to a low current or power density) of a kinetics field and may be visible to it, even if the polarization curve measured to each of three layers assumes the same structure as a result of the thickness of a different layer, in an ohm and the limited field of transportation, its possibility of differing considerably is high. As the substitute technique, the same amount of support (mgPt/cm<sup>2</sup>) can be attained to Layer B as the last example described by [ on C ] using the layer (namely, A) of Pt and half thickness 40%. If the usage of Pt same 20% as Pt on C is assumed to Pt 40% (namely, the same movement engine performance of an electrode catalyst), as for the engine performance in higher current density and power density on C, the thing on C layer excelled more will be expected to Pt 40% (others are the same). Therefore, it is clearly important to optimize the usage of Pt in higher Pt mass support, and to optimize the thickness of a layer to coincidence.

[0250]

A typical electrode catalyst bed may have the presentation covering Pt support on 1% of the weight of very low carbon, such as Pt, (for example, an electrochemistry sensor is received) on C from pure Pt black (for example, application of DMFC and an electrochemistry sensor). The thickness of the usual layer can change by 1-100 micrometers.

[0251]

By comparing drawing 23 with drawing 24 shows the example of this balance. In drawing 23, a polarization curve is the thing of the catholyte on the carbon which has the thickness (laydown) of Pt of 0.2 mgPt/cm<sup>2</sup> in cathode which consists of Pt 20% of the weight. In drawing 24, 5wt.%Pt on the carbon which has the thickness of 0.1 mgPt/cm<sup>2</sup> was used. The latter support is very low support, in order to attain the engine performance

shown by the polarization curve as compared with the electrode catalyst manufactured as usual. These measurement was performed by the zero gas which uses NAFION(trademark)112 film and uses 50-degree C H<sub>2</sub> and air.

[0252]

The related effect to the engine performance in higher current density is the pore structure of the carbon used in order to support Pt. This has the dramatic effect to an ohm property and transport properties. This mode of this invention is shown in drawing 25 . Although this drawing has the same amount of Pt support, the thickness of the same layer, and the same Measuring condition, it shows the difference in the polarization curve of oxygen and air to two catalyst powder which has different carbon support matter. The improvement in the engine performance is measured by difference smaller than that of the electrical potential difference of oxygen and air gas (that is, a smaller number is more good). Therefore, it is SHAWINIGAN so that a plot may show. The carbon support of the alternative which is BLACK is VULCAN (trademark). It is better than XC-72.

[0253]

About use of the spraying approach by complicated multicomponent, a complex particle including an electrode catalyst, carbon, the hydrophobic polymer, the proton transfer polymer, and this invention that generates other components, it is not indicated by the Prior art. This invention relates to the usage of the spraying conversion which generates the particle which has a useful complicated presentation although MEA is manufactured in application of a fuel cell.

[0254]

As argued above, MEA is oftenest built from a particle (electrode catalyst which consists of the metal and the carbon powder of electric conductivity which were supported on carbon), and the suspension of a colloid substance (liquid containing NAFION (trademark)), and the polymer matter (PTFE suspension of various liquids). This present pallet of the matter which the designer of MEA has to choose is limited very much. It is very advantageous to have other initiation matter which enables manufacture of MEA which has the property of coping with the problem which summarized above combining these matter by various methods.

[0255]

Drawing 26 is drawing showing the particle presentation structure which can be manufactured by this invention. Structure contains the electrode catalyst particle distributed to the polymer matrix. The secondary structure of an electrode catalyst particle is micron size. On the other hand, particle size is dozens to hundreds of nanometers, and the primary carbon support particle is decorated with the cluster of noble metals (qualification). A polymer is distributed in a particle.

[0256]

An ideal layer (cathode) is notionally shown in drawing 27 . Ideal solution must offer some descriptions. Enabling transportation of an electron as said description, the connection path of the conductive carbon particle from a gaseous diffusion layer (support to noble metals); It makes it possible to convey a hydrogen ion to an electrode catalytic site, The connection path of a proton transfer polymer (for example, NAFION (trademark)); by enabling water to escape The hydrophobic path which avoids that the water generated in the catalytic site overflows; Make it possible to convey a proton to a reactive site easily. The electrode catalyst metal exposed to the proton transfer polymer; Make it possible to convey an oxygen gas to all the locations of an electrode from gaseous diffusion equipment. There is an opening of a detailed scale etc. rather than it can set to the floc of the electrode catalyst which makes it possible to convey pore; and oxygen large enough to a reactive site in a shorter distance. The existing trial which attains this ideal situation is barred that processing particles run short and by restricting a printing process depending on the class of usable matter, and the class of structure guided from the conventional matter. MEA is manufactured from the particle of the noble-metals presentation which conductive carbon, such as current, Pt, and Pt alloy, supports. This matter must be combined with other various matter by the complicated MEA manufacture recipe, in order to try forming the idealized structure which summarized above. However, the property of these particles does not only enable easy manufacture of the optimal structure.

[0257]

It is very advantageous that it is usable in the complicated particulate structure containing the following.

- Condensation-ized Pt/C -PCP-Pt/C (PCP= proton transfer polymer)
- PTFE-Pt/C (PTFE= polytetrafluoroethylene polymer)



- PCP-PTFE-Pt/C -Pt/C (proton transfer and electric conductive polymer)

The example of the above particulate structure is shown in drawing 28 - drawing 30 . A PTFE-Pt/C (hydrophobic polymer) polymer qualification particle offers the following advantages. The hydrophobic matter is already built into powder, it is not necessary to mix behind, and good control is enabled [ rather than ] to hydrophobic uniformity. The same advantage mentioned above to the structure of having this polymer is also found. In addition to the advantage mentioned above, PCP-Pt / C (proton transfer polymer) polymer qualification particle offers the following advantages. PCP is included in the polymer which conveys a proton to a reactive site, and the secondary structure which offers close contact of a reactive site. A PTFE-PCP-Pt/C polymer qualification particle combines the advantage of all the matter mentioned above, and offers possibility of manufacturing an electrode with the single matter. Finally, the function of PCP and PTFE is combinable with one by using the polymer which are an electron and the conductor of both protons.

[0258]

A polymer qualification particle is generated by the spraying conversion which dissolves in a liquid and is started from the ingredient of the suspended particle. As a liquid forms a globule, it is atomized, and subsequently, a globule is heat-treated and forms a final particulate structure. It is possible to form the Pt/C particle of high quality beforehand, to make a liquid suspend them with other desirable components, to carry out spraying processing subsequently, and to form the detailed matter.

[0259]

Moreover, this invention is applicable to manufacture of a super capacitor. The main constraint to the life of a cell is the peaking capacity business that energy are recording of a cell is consumed by burst of high power. The one technique of solving this problem is that a cell copes with low-power output business, and a super capacitor offers the separate energy are recording unit when the peaking capacity pulse of short duration can be offered, and a power supply unit.

[0260]

A super capacitor is a capacitor of the type which accumulates energy into the electrochemistry duplex layer of the interface of an electrode/electrolyte. A super capacitor has power density far higher than the conventional cell, can accumulate far more much energy about weight and the volume, and can also send the energy over a period longer than a high discharge rate or the usual capacitor. When it is used combining a cell, it can become an energy source efficient to the altitude accompanied by a high current. Some of advantages which a super capacitor has to the conventional cell are as follows. That is, the high discharge current can sometimes be offered [ that it can charge and discharge almost without any restriction, that a discharge rate is high, and ].

[0261]

a super capacitor -- essential -- an electric double layer capacitor (EDLC) -- it is -- an electrolyte -- a conductor -- when the matter is contacted, separation of the charge to produce is used. Exhausting [ in the electrode produced by the source of an external output / an electron / exhausting / are recording or ] is offset by electrolytic ion chemical species. Since the order of molecular size has separation of the charge in these systems, the capacitance per [ which is produced as a result ] unit area is large. I hear that it cannot be carried out if an interface is crossed, therefore the advantage of the super capacitor to a cell can send a cycle called what 1 million, and migration of mass or a charge can maintain a high current drain and cycling effectiveness, and there is. However, constraint of a double layer capacitor is an electrical potential difference with a low cel from which it is restricted to 1V in an aquosity electrolyte, and it is restricted to 2.5V with an organic electrolyte. Higher capacitance is obtained with a high surface area electrode. Furthermore, a porous electrode provides altitude with the effective-surface product of the bigger interior. Therefore, carbon is high surface area, and since cost is cheap and easily available, it is common matter used as an electrode.

[0262]

Metallic oxides, such as RuO<sub>2</sub> and IrO<sub>2</sub>, were studied as a potential candidate of an electrode. The cycle voltamogram of RuO<sub>2</sub> is a rectangle mostly like the usual capacitor because of a series of oxidation reduction reactions produced with this metallic oxide. RuO<sub>2</sub> from which the specific high capacitor was created by 750 F/g extent at low temperature was reported. However, the cost of these electrodes was a limit factor in order for these electrodes to have grown quickly in the commercial scene. The electrolyte of a super capacitor can be used as a water acid or a water organic electrolyte. The advantage of an organic electrolyte is being able to attain a higher electrical potential difference. Although the electrical potential difference which an aquosity

electrolyte offers is more small, it has cheaper and higher conductance.

[0263]

The electrode of the super capacitor by this invention is RuO<sub>2</sub> and nH<sub>2</sub>O (it is a hydroxylation ruthenium hydrate (hydrous ruthenium hydroxide).) distributed on the carbon of high surface area. The hydration ruthenium oxide phase of 50:50 Pt-Ru / carbon black catalyst plays a role of methanol electrical-and-electric-equipment oxidation of a direct methanol fuel cell, and hydro-acid-izing of the proton exchange film fuel cell which uses reformed gas as a fuel.

[0264]

The super capacitor matter can be manufactured as a printing layer on the proton transfer polymer film (NAFION117 (trademark) etc.) which acts as an electrolyte, a separator, and an inter-electrode glue line. The property of a super capacitor is adjusted so that it may have consistency in a property required for the high peaking capacity of a cell. Consequently, a super capacitor has the small volume and is formed appropriately [ although / unifying in a hybrid power unit / an effective-output consistency is high ].

[0265]

(Example)

The above description and the following examples are referred to by using a trade name for the illustration of some matter of the matter. However, the operation gestalt of this invention is not limited to using such specific matter.

[0266]

for example, TEFLON (trademark) (Du Pont (E. I. duPont de Nemours) [U.S. Delaware Wilmington (Wilmington) whereabouts]) -- a hydrophobic polymer -- more specifically, a tetrafluoroethylene fluorocarbon polymer is pointed out. NAFION (trademark) (Du Pont (E. I. duPont de Nemours) [U.S. Delaware Wilmington (Wilmington) whereabouts]) points out a hydrophobic proton transfer polymer, and, specifically, points out a sulfuration fault fluoro hydrocarbon (sulfurated perfluorohydrocarbon) polymer.

[0267]

Moreover, refer to the carbon of various gestalten for this publication and an example by referring to a trade name. The general properties of such carbon support are enumerated to Table 2. SHAWINIGAN BLACK (trademark) is available acetylene black from Chevron Chemical (Chevron Chemical Co.) [the U.S. Texas Houston (Houston) whereabouts]. VULCAN (trademark) XC-72 are available from KABOTTO (Cabot Corp.) [the U.S. Georgia alpha RETTA (Alpharetta) whereabouts], and available with the gestalt of graphite. Norit (NORIT) SA-3 are activity carbon too available from KABOTTO (Cabot Corp.) [the U.S. Georgia alpha RETTA (Alpharetta) whereabouts]. PWA is available activity carbon from a KYARU gon carbon company (Calgon Carbon Corp.) [the U.S. Pennsylvania Pittsburgh (Pittsburgh) whereabouts]. BLACKPEARLS (trademark) is available from KABOTTO (Cabot Corp.) [the U.S. Georgia alpha RETTA (Alpharetta) whereabouts], and its KETJENBLACK (trademark) (trademark) is available from the Akzo novel (Akzo Nobel) [the Netherlands and the AMERUSU fault (Amersfoort) whereabouts].

[Table 2]

表 2. 触媒支持体として使用されるカーボンブラック

カーボン源	粒径 (マイクロメートル)	BET 表面積 (m <sup>2</sup> /g)
SHAWINIGAN Black (R)	0.055	80
VULCAN (R) XC-72	0.039	240
グラファイト化 VULCAN (R) XC-72	0.5 *	100 *
ノリット SA-3	22	700
PWA	22	820
BLACKPEARLS (R)	0.4	1400 *
KETJENBLACK (R)	0.4	1400 *

\*これらの値は概略値

GURAH0 1300 (GRAFO1300) and GURAH0 1322 (GRAFO1322) are water nature powder which contains

20 % of the weight and 22% of the weight of carbon, respectively, and are available from the Fuchs lubricant (Fuchs Lubricant) [the U.S. Illinois Harvey (Harvey) whereabouts]. In order to help the long term stability of these carbon distributions, the binder system which uses the same cellulose as the base was used for GFAFO suspension. It decomposes at about 300 degrees C, and this binder has long storage stability. GFAFO1300 is SHAWINIGAN. It is distribution of BLACK (trademark) and GURAH0 1322 is VULCAN (trademark). It is distribution of XC-72.

[0268]

These GFAFO distributions are alkalinity slightly and pH is about 9. Because of the property of a binder, it is stable by about six or more pH. When this created a Pt/C electrode catalyst as a platinum precursor using Pt (NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>, since the salt which dissolved had neutral pH, it was not a problem.

[0269]

1. MnOx/C support electrode catalyst particle Two groups of the example of a MnOx/C complex electrode catalyst were first prepared by this invention. The 1st group who showed in Table 3 was prepared generation of ultrasonic aerosol, and by heating aerosol in a hot wall reactor (tube furnace). The 2nd group who showed in Table 4 was prepared using the spraying nozzle, in order to generate the aerosol heated in the spray drier. Air was used as carrier gas in all the examples.

[Table 3]

表 3. 超音波で生成された電極触媒のための実験条件

実施例 番号	前駆体	追加界面活 性剤	リアクター 温度 (°C)	Mn (wt. %)	前駆体温 度 (wt. %)
19A	KMnO <sub>4</sub>	なし	400	10	5
19B	Mn 窒化物	なし	350	10	5
20A	KMnO <sub>4</sub>	なし	350	10	5
20B	KMnO <sub>4</sub>	なし	350	10	5
23A	KMnO <sub>4</sub>	0.017	350	10	5
24A	KMnO <sub>4</sub>	0.034	350	10	5
27A	Mn 窒化物	0.049	350	10	5
28B	KMnO <sub>4</sub>	0.049	300	10	5
28D	KMnO <sub>4</sub>	0.049	250	10	5
28E	KMnO <sub>4</sub>	0.049	200	10	5
29B	Mn 窒化物/ KMnO <sub>4</sub>	0.012	350	10	5

[Table 4]

表 4. スプレーノズルで生成された電極触媒のための実験条件

実施例番号	前駆体	追加界面活性剤 (wt. %)	リアクター温度 (℃)	Mn (wt. %)	前駆体濃度 (wt. %)
30A	KMnO <sub>4</sub>	0.078	208	10	5
30C	KMnO <sub>4</sub>	0.078	208	10	5
34B	KMnO <sub>4</sub>	0.078	208	10	5
41A	KMnO <sub>4</sub>	0.083300	315	10	5
41B	KMnO <sub>4</sub>	0.006700	315	10	5
41C	KMnO <sub>4</sub>	0.083300	315	20	5
41D	KMnO <sub>4</sub>	0.083300	315	10	5
44B	なし	0.000000	208	—	5
44C	KMnO <sub>4</sub>	0.001600	208	5	5
44D	KMnO <sub>4</sub>	0.001600	149	5	5
44E	KMnO <sub>4</sub>	0.001600	149	10	5
44F	KMnO <sub>4</sub>	0.001600	208	10	5
44G	KMnO <sub>4</sub>	0.001600	208	10	5
47A	なし	0.000000	208	—	10
47B	なし	0.000000	208	—	5
47C	なし	0.000000	208	—	2.5
47D	KMnO <sub>4</sub>	0.000000	208	10	2.5
47E	KMnO <sub>4</sub>	0.001600	208	10	2.07

[0270]

The carbon precursor of all examples enumerated to Table 3 and 4 was GFAFO1300. Water nature powder also contains an anionic surfactant. The amount of additions of an anionic surfactant (TRITON(trademark) X-405, sigma -ORUDO rich (Sigma-Aldrich) the [U.S. Missouri St. Louis (St.Louis) whereabouts]) was added to some of examples, as shown in Tables 3 and 4. TRITON (trademark) X-405 is the 70-% of the weight solution of the polyoxyethylene (40)-iso octyl phenyl ether dissolved in water. GFAFO1300 is suspended in water, and Mn precursor dissolved in water before is slowly added to carbon suspension, agitating. Precipitate is reduced, when a surface active agent is added to carbon suspension in front of Mn precursor and Mn precursor is added. Although the reaction temperature of all examples is maintained lower than about 400 degrees C, the temperature (for example, it exceeds about 600 degrees C) the reason is too high is because the burn off of the carbon may be carried out, when air is used as carrier gas.

[0271]

For spraying nozzle generation (Table 4), the batches of MnOx/C powder are the following methods and, more specifically, were prepared by the spray dryer. 35.6kg (78.3lbs) carbon paste was added to batching tubing. Subsequently, 65kg (143lbs) deionized water was added to carbon paste, and was mixed completely. The 0.13kg (0.286lbs) nonionic surfactant was added to mixture, and mixture was agitated for about 10 minutes. With another tubing, 2.27kg (5lbs) potassium permanganate (potassium permanganate) was dissolved by 65kg (143lbs) deionized water. The solution was mixed for 20 minutes, as dissolved in KMnO<sub>4</sub>. Subsequently, KMnO<sub>4</sub> solution was slowly added to carbon paste.

[0272]

Drawing 31 shows the scanning electron microscope (SEM) microphotography of example 23A (Table 3). The particle mol follow G shown in drawing 31 is common to the sample generated with the supersonic wave. A particle has a spherical configuration and the particle size of a particle changes between about 0.3 micrometers and 10 micrometers. A support phase consists of a first-class carbon particle. As for transmission electron microscopy (TEM), the support phase showed that it had a vesicular structure.

[0273]

Smaller floc can be made to dissociate a particle partially according to mechanical force, such as compressing a particle, by rolling out in a supersonic wave or a layer. Drawing 32 and 33 show ultrasonic induction

dissociation to the usual electronic catalyst powder generated by ultrasonic generation. Drawing 32 shows the particle size distribution before destroying an aggregated particle by SONIFIKESHON, and drawing 33 shows the same powder after SONIFIKESHON.

[0274]

Drawing 34 shows the particle size distribution of spray drying powder. Although an aggregated particle is more large and it has the diameter of a maximum of 20 micrometers, powder has the mean particle diameter of about 5 micrometers. The difference of an aggregated particle is related to the particle size of a globule typical to the two aerosol generation technique.

[0275]

The BET nitrogen absorption process was used and a supersonic wave, the surface area of the electrode catalyst powder generated by the spraying nozzle, and voidage were measured. A result is summarized to Table 5. When the sample generated ultrasonically is compared, it is clear conversion temperature's to affect surface area.

Although example 19A is changed at 400 degrees C and it has the surface area of 93m<sup>2</sup>/g, on the other hand, 19B is changed at 350 degrees C, and has the surface area of 37m<sup>2</sup>/g. However, even if it lowered temperature to 300 more degrees C and 250 degrees C, catalyst surface area did not decrease remarkably.

[0276]

Moreover, it is clear that existence of a surfactant affects surface area. In the same conversion temperature, the sample (example 29B) which has an additional quantity of a surfactant in a precursor solution has surface area smaller 40% than the same powder (example 19B) which does not have an additional surfactant.

[Table 5]

表 5. 電極触媒の表面積

実施例	生成方法	BET 表面積 (m <sup>2</sup> /g)	平均細孔直径 (nm)
19A	超音波	93	-
19B	超音波	37	-
28B	超音波	19	-
28D	超音波	24	-
28E	超音波	19	-
29B	超音波	25	-
34B	超音波	21	-
41A	スプレーノズル	21	-
41B	スプレーノズル	21	-
41C	スプレーノズル	17	-
41D	スプレーノズル	22	-
44C	スプレーノズル	28	20
44D	スプレーノズル	29	19
44E	スプレーノズル	24	17
44F	スプレーノズル	24	20
44G	スプレーノズル	24	21
44H	スプレーノズル	36	9
47A	スプレーノズル	36	23
47B	スプレーノズル	36	23
47C	スプレーノズル	33	23
47D		24	18
47E		25	16

The sample of the pure carbon which does not contain a surface active agent has the surface area of the highest about 35m<sup>2</sup>/g. Therefore, when the precursor of MnOx exists in a solution, surface area becomes small, the surface area of the sample containing Mn is in the order of 20-25m<sup>2</sup>/g, and this is equal to the surface area of the sample ultrasonically generated in the same conversion temperature.

[0277]

Therefore, although the selected aerosol generation method mainly affects distribution of particle size, on the other hand, conversion temperature mainly affects the surface area of a MnOx/C particle. However, the effectiveness of conversion temperature over the surface area in temperature lower than 300 degrees C is the minimum. A remarkable change was not observed by the pore particle size distribution of a catalyst as a function of a preparatory condition. To all spraying nozzle generation samples, average pore particle size is 20-nanometer order, and this shows a secondary carbon support phase without significant micro voidage.

[0278]

Moreover, XPS analysis was also carried out to these MnOx/C powder. XPS (X-ray photoelectron spectroscopy) analysis offers the surface presentation of an electronic catalyst, and the information about the oxidation state of Mn. It was analyzed in order that the three properties of a XPS spectrum might compare the sample generated under different conditions.

[0279]

1) Mn which shows the oxidation state of Mn Location of the binding energy of 2p<sub>3/2</sub> photoelectron;  
2) Mn [ between / samples / directly / for the count which used as the base the model of the mean diameter of MnOx which MnOx distribution directed or distributed ] 2p -- 3/2 and C Relative intensity [ of 1s photoelectron peak ];

[0280]

3) O related to O<sub>2</sub> combined with O<sub>1</sub> and Mn which were combined with C support, and O<sub>3</sub> combined in the surfactant used for precursor formation Ratio between the binding energy with which photoelectron peaks differ for 1s.

[0281]

Two catalysts marketed were evaluated for the comparison with the powder of this invention. Each was standard MnOx/C powder used [ in / it is available and / the applicable field of a zinc air battery ] from a commercial manufacturer. Since the oxidation state of Mn in an electrode catalyst was specified, the three standard substance was also analyzed. (MnO<sub>2</sub> powder, 2OMn<sub>3</sub> powder, and KMnO<sub>4</sub> powder) .

[0282]

Record of a preparatory condition and a spectrum and data processing were the same to all samples. The sample was prepared for XPS analysis by pushing in in the indium (In) foil (99.9%) washed in HNO<sub>3</sub> in powder before in order to remove the impurity of surface C and O.

[0283]

The XPS spectrum of three control samples (Mn 2O<sub>3</sub>, MnO<sub>2</sub> and KMnO<sub>4</sub>) and all electrode catalyst powder is AXIS which uses an aluminum anode plate (aluminum K $\alpha$ =1486.7eV, 225W), and functions in the deltaE= fixed mode of 80eV pass energy. It was recorded on the HSi (Kratos Analytical) spectrometer. The remaining pressures of a chemical laboratory were 1x10<sup>-9</sup>Torr(s). The location of a peak is C. It was presumed to 1s=284.6eV binding energy. The peak of following XPS shown with electronic level, i.e., Mn, 2p, C 1s, O 1s and K 2p was recorded. One investigation scan was gained in the range of 75-1175eV binding energy to a control sample and electrode catalyst powder, before the high resolution spectrum was gained. The reinforcement of an experiment was presumed from the field of a corresponding peak measured about the peak of smooth origin. Mn It is K as 2p. The peak field of the peak of 2p includes the field of the peak of both 2p<sub>3/2</sub>, and 2p<sub>1/2</sub>.

[0284]

A spectrum is gained to a control sample and shows the result in Table 6. Mn in the XPS spectrum of KMnO<sub>4</sub> The peak of 2p<sub>3/2</sub> consists of two peaks, therefore two different oxidation states of Mn exist.

[Table 6]

表 6. コントロールサンプルの XPS データ

サンプル	Mn 2p <sub>3/2</sub>	O 1s (eV)	K 2p <sub>3/2</sub>	C 1s (eV)
Mn <sub>2</sub> O <sub>3</sub>	641. 6	529. 6	-	284. 6
MnO <sub>2</sub>	641. 8	529. 4	-	284. 6
KMnO <sub>4</sub>	641. 5	529. 8	290. 8	284. 6
	644. 0		293. 0	



Mn As for the reference data about the binding energy of 2p<sub>3/2</sub>, it is shown as follows that binding energy is dependent on the oxidation state of Mn.

[0285]

Mn (II) Inside of MnO 640.6eV Mn (III) Inside of Mn<sub>2</sub>O<sub>3</sub> 641.6eV Mn (IV) Inside of MnO<sub>2</sub> 642.6eV Increase of XPS binding energy when the oxidation state of a component is progressing is an inclination generally observed to various matter. The oxidation state of Mn in Mn<sub>2</sub>O<sub>3</sub> is Mn (III), and in MnO<sub>2</sub>, since it is Mn (IV), the latter binding energy should become larger than the former compound. However, experimental data is Mn in the control sample of Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>. The same binding energy (within the limits of an experimental error) is shown to 2p<sub>3/2</sub> photoelectron.

[0286]

However, since MnO<sub>2</sub> is a powerful oxidizer, it does not hit that it is surprised that the average oxidation state of Mn near a front face is inferior to Mn (IV). In other possible reasons, the reduction guided to the X-ray breaks out to MnO<sub>2</sub> powder exposed to the X-ray beam.

[0287]

In the result of XPS of a more than, the oxidation state of Mn (III) and Mn (IV) shows clearly that it is undistinguishable. However, the general inclination over bigger binding energy shows the oxidation state of higher Mn.

[0288]

Mn to Samples 1A and 2A whose table 7 is two electrode catalyst samples marketed 2p -- 3/2O 1s and C The information about the binding energy for 1s is included.

[Table 7]

表 7. 市販の電極触媒のサンプルの XPS データ

サンプル	Mn 2p <sub>3/2</sub> ピーク位置 (eV)	K 2p <sub>3/2</sub> ピーク位置 (eV)	O 1s ピーク位置 (eV)
1A	642. 3	292. 2	529. 7-57% 532. 1-43%
2A	642. 4	292. 7	529. 8-62% 531. 9-35% 534. 6-3%

Mn By 642.3eV and sample 2A, the comparison of the binding energy of 2p<sub>3/2</sub> is 642.4eV, and does not show the remarkable difference at sample 1A. This binding energy is higher than 641.6eV of binding energy observed to Mn (III) of a Mn<sub>2</sub>O<sub>3</sub> control compound 0.7eV. Mn observed to the electrode catalyst by which both are marketed According to reference data, the binding energy of 2p<sub>3/2</sub> is very close to the location of 642.6eV equivalent to Mn (IV) oxidation state. The X-ray induction reduction effectiveness observed to the MnO<sub>2</sub> control sample has very high possibility of saying that it is expressed smaller or does not exist at all to an electrode catalyst sample. It can distribute highly and MnO<sub>2</sub> chemical species which touch the conductive carbon front face closely can guess highly that it is hard to receive X-ray induction reduction from MnO<sub>2</sub> compound of a crystalline substance.

[0289]

Therefore, average Mn oxidation state of the electrode catalyst marketed is between Mn (III) (IV), and possibility of Mn (IV) is the highest. Mn The location of the binding energy of 2p<sub>3/2</sub> can be used as criteria for attaining the oxidation state of suitable Mn for the activity of an electrode catalyst, when evaluating the electrode catalyst by this invention. The oxidation state of Mn measured by XPS may differ from the oxidation state in an actual situation slightly.

[0290]

Table 8 includes the outline of XPS data over the examples 19A-34B (Tables 3 and 4) of an electrode catalyst. The XPS data of example 30D (what heated example 30A further to 250 degrees C in atmospheric air for 1 hour), and example 33A (what heated example 30A further to 170 degrees C in atmospheric air for 1 hour) are also contained.

[Table 8]

表 8. 電極触媒のサンプルの XPS データ

実施例	Mn 2p <sub>3/2</sub> ピーク位置 (eV)	K 2p <sub>3/2</sub> ピーク位置 (eV)	O 1s ピーク位置 (eV)
19A	642.4	292.6	529.9-59% 531.3-32% 533.0-9%
19B	642.0	293.0	529.8-21% 532.2-79%
23A	642.3	292.8	528.9-59% 532.2-41%
28D	642.3	292.8	530.0-30% 531.3-26% 532.9-44%
28E	642.1	293.1	529.9-22% 531.3-42% 533.1-36%
29B	641.4	292.9	-
30A	642.6	293.0	528.9-21% 532.2-79%
30C	642.2	292.8	528.9-21% 532.2-79%
30D	641.5	292.9	-
33A	641.3	293.0	-
34B	642.3	293.0	-

Mn of the sample obtained with Mn (NO<sub>3</sub>)<sub>2</sub> as a precursor (examples 19B and 29B) As compared with the electrode catalyst marketed, only 0.4eV - 1.0eV of the peak location of 2p<sub>3/2</sub> is low. Mn of most electrode catalysts 19A, 23A, 28D, 30A, 30C, and 34B 2p<sub>3/2</sub> binding energy are the same as that of the location of a commercial sample. For this result, the oxidation state of Mn in these samples is Mn (IV), and on the other hand, with the value of a Mn<sub>2</sub>O<sub>3</sub> control sample, since it is near, as for the oxidation state of Mn in Examples 19B and 29B, a binding energy value shows a near thing by Mn (III). Since Examples 19B and 29B make origin the formulation of the precursor containing Mn (NO<sub>3</sub>)<sub>2</sub> by contrast, KMnO<sub>4</sub> of bring [ the catalytic activity from which the formulation of a different precursor brings about a different MnOx surface chemistry kind in an electrode catalyst, therefore differs ] is clear. The most suitable possibility of the average oxidation state near Mn (IV) is high for the electrode catalytic activity of a sample about which it argues with electrode catalytic activity after this.

[0291]

Examples 30D and 33A compare with the considerable object with which it corresponds before heat treatment (example 30A), and it is lower Mn. About 1.0eV is shifted to 2p<sub>3/2</sub> binding energy. Mn (IV) is returned to the oxidation state of Mn (III) by the postheat treatment, therefore this shows that it may not be desirable.

[0292]

O of example 19A 1s spectrum is the property of the example which conversion of a precursor has completed. Therefore, different O to each sample The ratio of the peak of a photoelectron can be used for 1s, and the ratio of a MnOx crystal front face and the carbon carrier surface which is not covered with a MnOx crystal can be presumed. O Only 9% of 1s peak intensity can connect with existence of the oxygen from the surfactant which did not react during spraying conversion. About example 19B which is the case where others are restricted, it is 532.2eV O. 1s peak is O. About 80% of peak intensity is occupied for 1s, it corresponds to O of NO<sub>3</sub> chemical species, and the existence shows that the precursor is not changed completely. Example 19B shows remarkably more low electrode catalytic activity as compared with example 19A so that it may argue below.

[0293]

The only difference of the preparation conditions of Examples 19A, 28D, and 28E is spraying conversion temperature. O Significant O relevant to [ as compared with 1s field ] existence of a surfactant at example 19A (400 degrees C) Although a peak does not exist for 1s, at Examples 28D (250 degrees C) and 28E (200 degrees C), a peak (533.2eV) is O. 30 - 40% of reinforcement is occupied for 1s.

[0294]

Therefore, spraying conversion temperature affects existence of the surfactant of catalyst powder. Since the remaining surface active agent adheres on activity MnOx chemical species or a carbon front face, the catalytic activity of a sample may be affected potentially. Therefore, in order to suppress the final negative effectiveness of a surfactant to the minimum, higher conversion temperature should be used or existence of the surfactant in a spraying solution should be suppressed to the minimum.

[0295]

Moreover, XPS data also include the information about distribution of the MnOx chemical species on a carbon carrier surface. This information is indirectly included in the relative intensity of I (Mn 2p)/I (C 1s). In order to pull out the information about distribution, some of other parameters are required for the bulk presentation of a sample, BET surface area, the relative intensity theoretically calculated to monolayer distribution to an electrode catalyst.

[0296]

Table 9 includes the information about the bulk presentation of the sample analyzed by both atomic absorption spectroscopy (AAS) and the X-ray fluorescence method (XRF). Generally the data of XRF show a higher value to Mn and K as compared with AAS data. A result shows that the electrode catalyst powder of this invention has molecule concentration with both Mn and K higher than a commercial sample. The absolute value of the percentage-by-weight concentration by AAS to the electrode catalyst of this invention is strictly adjusted in the forecast based on the presentation of a precursor solution.

[Table 9]

表 9. バルク組成物の AAS/XRF データ

サンプルあるいは実施例	Mn (wt. %)	K (wt. %)	Mn/C 割合 × 10 <sup>2</sup>	K/C 割合 × 10 <sup>2</sup>
1A*	1.78/2.80	0.90/1.47	0.40/0.64	0.28/0.48
2A*	6.00/9.54	2.67/3.87	1.44/2.32	0.90/1.37
19A	9.04/14.8	7.94/12.2	2.38/4.43	2.93/5.13
19B	9.06/14.9	2.48/3.70	2.24/4.00	0.86/1.40

\* 従来技術

Table 10 includes the value calculated theoretically [ I(Mn 2p)/I (C 1s) relative intensity ], when it is the value by which the data about BET surface area, i.e., MnOx chemical species, were distributed as a monolayer, and I (Mn 2p)/I (C 1s) was measured experimentally.

[0297]

Commercial sample 2A contains high surface area activity carbon. All the electrode catalysts of this invention have the order of low surface area [ magnitude ], after primary quantity surface area carbon support forms secondary carbon support structure, as mentioned above. High surface area activity carbon support (samples 1A and 2A) has a micro opening by the very big degree. On the other hand, the spraying conversion secondary support formed of the above example mainly has a meso opening.

[Table 10]

表 10. MnO<sub>x</sub> 粒子径の推定の XPS モデルデータ

サンプル/ 実施例	I(Mn 2p)/ I (C 1s) (実験値)	I(Mn 2p)/ I (C 1s) (一層)	表面積 (m <sup>2</sup> /g)	推定粒子径 (nm)	300mA/cm <sup>2</sup> の 放電電流に 置ける電圧 (V)
1A*	0.378	0.205	121	不均一な分 散	—
2A*	2.803	0.340	713	不均一な分 散	0.82
23A	1.188	1.754	93	2	1.02
30A	0.863	6.651	24	15	0.91
30C	1.090	6.651	25	12	0.95
30D	0.688	6.650	30	40	0.76

\* 従来技術

The information about the average MnO<sub>x</sub> particle size expected is searched for by comparing the theoretical value and experimental value of I(Mn 2p)/I (C 1s) specific strength. Change of XPS specific strength and the comparison with experimental data and theoretical it are based on the approach of KERUKUHOFU (Kerkhof) and Maureen (Moulijn) (EFU . Py . Jay . em . KERUKIUHOFU (F. P.J.M.Kerkhof) and Jay . ray . Maureen (J. A.Moulijn), J.Phys.Chem. the 83rd volume, 1612 (1979) pages). This technique offers the information which is reliable about distribution of the active ingredient on distributed support, as before applied to the distributed catalyst (volume [ 161st ] (1997) 105 pages [ PIATANASOBA (PAtanasova) and tee . HARASHIEFU (T. Halachev), Applied Catalysis A;General 108 (1994) 123; Py . ata NASOBA et al. (P. Atanasova et al.), Applied Catalysis A;General ]). When the experimental value of I(Mn 2p)/I (C 1s) specific strength is lower than near, however it in the theory, anticipation of particle size is possible by this XPS model. When the experimental value of I(Mn 2p)/I (C 1s) specific strength is higher than a theoretical value, an exact particle size cannot be expected with this XPS model. However, distribution of the MnO<sub>x</sub> kind which this has in the outer surface of carbon support alternatively suggests that it is heterogeneity.

[0298]

With Samples 1A and 2A, the experimental value of I(Mn 2p)/I (C 1s) specific strength is notably higher than the theory. Therefore, localization of the MnO<sub>x</sub> active species is carried out mainly on the outer surface of carbon support, without using all the front faces of carbon support effectively. Since the front face of activated carbon contains most quantity of micropore, this result is not a surprising thing. Between the wet processes used in order to form such powder, this porosity gets wet and it is hard to use it for adsorption of the precursor from the liquid phase for a property.

[0299]

By contrast, the experimental value of the I(Mn 2p)/I (C 1s) specific strength of the electrode catalyst of this invention was lower than the theoretical value, and from the deflection, as a detail was shown in Table 10, the mean particle diameter of MnO<sub>x</sub> was expected about each sample. Anticipation mean particle diameter changes from 2 nanometers of example 23A to 40 nanometers of example 30D. As for the result of example 23A, active species adhered to homogeneity over the whole front face of carbon support, and it has suggested that a MnO<sub>x</sub> surface kind is the monolayer of several [ only ] layers. Distribution changes with the conditions of preparation and it is clear that its a related parameter is the class and spraying conversion temperature of spraying generation. However, the data of a XPS model express that adhesion is homogeneity over the carbon carrier surface.

[0300]

Table 10 also includes the information about the test of an electrode catalyst again. In the half-cel experiment by discharge current 300 mA/cm<sup>2</sup>, the electrical potential difference which reached with the electrode prepared with the electrode catalyst of this invention was chosen as a parameter which measures whenever [ electrode catalytic activity / of a catalyst ].

[0301]

Drawing 35 shows correlation with the activity of an electrode catalyst, and the XPS anticipation mean particle diameter of the data of Table 10. Linear correlation is between the electrode catalyst engine performance of a catalyst, and the average microcrystal size of MnOx. All the catalysts (except for example 30D) compared by drawing 35 are the same Mn. This wants to have  $2p_{3/2}$  binding energy, and to mention having suggested that the oxidation state of Mn is the same especially. Cluster size of MnOx of a commercial catalyst was not able to be expected based on the XPS model. If it is in why, it is because they were distributed over the ununiformity and MnOx had adhered to the outer surface of support alternatively. However, if the electrode catalyst engine performance of a sample 2A catalyst is compared with the data in drawing 35, the size of MnOx corresponding to this electrode catalyst will be about 30 nanometers.

[0302]

The combination of the information about the oxidation state of Mn and distribution of MnOx drawn from XPS analysis is the information source which has value in clarifying structure of a MnOx/C electrode catalyst and predicting the engine performance of an electrode catalyst. It is the probably most important requirement to acquire the oxidation state of Mn optimal for the engine performance of an electrode catalyst. However, it is also important to form active species in the form which raised distribution. It exposes to an electrochemical reactant and the number of the active centers which do the catalysis of a reaction increases, so that distribution is high.

[0303]

In order to check the average microcrystal size expected by XPS, some other analytical skill was used. The X diffraction (XRD) spectrum of a collating sample prepared by ultrasonic generation of  $\text{KMnO}_4$  at 300 degrees C as a precursor of MnOx showed nothings that suggest the crystal structure. Generally, such a kind was not formed or this result has suggested that that concentration and/or size were too small for detecting by XRD. Generally, the XRD limit of detection of a distributed oxide is about 40-50 nanometers in microcrystal size. Some crystal structures were observed by the catalyst (conversion temperature of 300 degrees C) of the Mn (NO<sub>3</sub>)<sub>2</sub> base. However, this may relate to existence of Mn (NO<sub>3</sub>)<sub>2</sub> from which it is not changed in a catalyst so that the description may be too weak for identifying and XPS data may suggest.

[0304]

When conversion temperature was raised further, the clearer XRD peak was generated and the location was a thing concerning formation of the crystalline substances [ Mn / Mn and / 2O<sub>3</sub> ] 3O<sub>4</sub>. Generally, if this has too high conversion temperature, it will suggest that big microcrystal detectable by XRD is formed of diffusion and condensation of the MnOx kind changed (by residence time same except this point). If such [ once ] a low decentralized structure is formed, electrode catalytic activity is not greatly expectable. Therefore, the conversion rate and diffusion rate of the activity surface kind optimal for the engine performance of an electrode catalyst are securable with some suitable combination of a spraying generation parameter, such as a generation method of spraying, a presentation of a precursor, and conversion temperature.

[0305]

It is related to the advantage of the data of distribution by XPS being the information averaged about many catalyst particles. TEM which gives the mol follow G of a catalyst by the image of a high scale factor is used in order to check the data collected by XPS. In example 23A, the small amorphous MnOx kind whose size is 1-2 nanometers was observed on the primary carbon particle front face ( $d=30\text{nm}$ ). It was checked that these kinds are distributed over the whole particle by the surface kind at homogeneity by the energy dispersion spectrometry (EDS) carried out to the particle including Mn.

[0306]

The TEM image of sample 2A showed the field of high contrast resulting from MnOx which adhered mainly to the outer surface of carbon support. These MnOx kinds of size of the image of a high scale factor was 20-40 nanometers, they are crystalline substances and existing in the outer surface of carbon support was shown. Therefore, the XPS data about a MnOx distribution object and the homogeneity of an affix were checked by TEM observation. TEM observation of sample 1A showed the same result.

[0307]

Moreover, TEM observation of example 30D which carried out the postheat treatment of the sample corresponding to example 30A was also performed. As indicated to Table 10, the XPS anticipation particle size

of example 30A was about 10-15 nanometers, and, on the other hand, was about 40 nanometers in example 30D. Many MnOx clusters are distributing in some fields of carbon support, and big microcrystal with a size of about 50 nanometers forms the TEM image in other fields. A big cluster consists of MnOx microcrystal and the size is about 10-15 nanometers.

[0308]

This TEM observation has the XPS anticipation mean particle diameter of 40 nanometers, and a good correlation. In addition, it points out that MnOx microcrystal can be diffused, big microcrystal can be formed and these results can decrease an activity phase remarkably by the elevated-temperature after treatment of the very important matter about the structure of the electrode catalyst of this invention, i.e., a catalyst. If it connects to change of the oxidation state of Mn observed by XPS, this will serve as explanation with the electrode catalytic activity of the sample which carried out the postheat treatment clear [ that it is remarkably low compared with the contrast in which origin carried out spraying conversion ].

[0309]

Existence of the spraying conversion temperature given to the activity of an electrode catalyst and a surfactant, the concentration of a precursor, and the effect of an additive were systematically analyzed in the Examples 41A-47E. Based on the knowledge of former XPS, the sample was characterized as the thing which expresses the oxidation state of Mn for the binding energy location of Mn, and a thing which measures distribution of a MnOx kind for I(Mn) I [ / ] (C) specific strength. Specific strength and O The XPS peak for 1s was analyzed about whenever [ effect / on existence of a surfactant and its electrode catalytic activity ].

[0310]

Drawing 36 expresses the relation between the electronic activity of Examples 19A-30D, and XPS specific strength. This dependency was used as the datum line for analyzing further the effect affect the electronic activity of a different spraying conversion parameter. With no samples generated by spraying conversion, BET surface area is similar and big effect will give XPS model count of the average size of a MnOx cluster. Therefore, it can become distributed measurement of active species enough to measure the I(Mn) I [ / ] (C) specific strength of XPS. If other properties (surface area and Mn oxidation state) of a catalyst are the same so that drawing 36 may see, the engine performance of the electrode catalyst of a sample is so high that I(Mn) I [ / ] (C) specific strength is high.

[Table 11]

表 1 1. 実施例 41A から 47E の XPS データ

実施例	スプレー 転化温度 (℃)	Mn (wt. %)	前駆体 濃度 (wt. %)	Mn2p <sub>3/2</sub> 結 合エネル ギー (eV)	I (Mn 2p) / I (C 1s) (実験 値)	300mA/cm <sup>2</sup> の放電電 流に置け る電圧 (V)
41A	315	10	5	642.2	0.71	0.91
41B	315	10	5	642.0	0.83	0.97
41C	315	20	5	641.9	1.39	0.85
41D	315	10	5	641.8	1.03	0.96
44C	208	5	5	641.7	0.33	0.99
44D	149	5	5	642.3	0.46	0.92
44E	149	10	5	642.3	1.03	1.01
44F	208	10	5	642.3	0.76	0.95
44G	208	10	5	642.2	0.86	1.00
47D	208	10	2.5	642.4	0.78	0.95
47E	208	10	2.1	642.2	0.86	0.97

Mn of most samples 2p<sub>3/2</sub> binding energy are the same as that of the electrode catalyst (642.3\*0.1eV) analyzed before, and this shows the oxidation state of Mn (IV). From the location of the above [ binding energy ], only Examples 41C-44C shift remarkably, and are 641.8\*0.1eV. Therefore, with the latter sample,



the oxidation state of Mn is low and possibility of being mixing of the oxidation state of Mn (IV) and Mn (III) is high.

[0311]

Examples 41A-41D show change to various amounts of the surfactant in a spraying solution, and weight [ of Mn ] %, and the effect of spraying conversion temperature compared with Examples 31A and 30C. If example 30C is compared with example 30C41A, high conversion temperature will reach the conclusion that it is not necessarily useful for the mol follow G and the engine performance of a catalyst. In example 41A which kept other parameters constant and was carried out at high conversion temperature, the activity of MnOx distribution and an electrode catalyst is low.

[0312]

It is clear that the engine performance of dispersibility and an electrode catalyst is so good that the amount of the added surfactant is low (please compare example 41A with example 41B). It does not become improvement in the electrode catalyst engine performance as for twice about the concentration of Mn. On the contrary, the electrode catalyst engine performance at the time of doubling the concentration of Mn is the lowest in a series of spraying generation samples. This result is 10% of the weight of Mn surface coating, and the carrier surface product of about 25m<sup>2</sup>/g, and has suggested that distribution of a good MnOx kind and the carbon carrier surface product which is not covered have balanced enough. Even if it increases Mn concentration further, and it may make concentration based on MnOx(es) high, the engine performance of an electrode catalyst does not improve.

[0313]

The preparation conditions of Examples 41A and 41D are the same except that example 41D lessens the flow rate to a spraying reactor. In example 41D, it is distinct that whenever [ distribution and electrode catalytic activity / both ] is improving. This effectiveness is a mean in whenever [ electrode catalytic activity ] greatly (30% or more) at distribution. The long residence time should care about making the oxidation state of Mn low like example 31D which carried out the postheat treatment. If the residence time is lengthened at an elevated temperature, the reduction which a MnOx surface kind does not have will break out.

[0314]

Although distribution of active species became good in the comparison with example 44C and example 44D both of whose Mn concentration is 5 % of the weight when conversion temperature was lowered to 149 degrees C from 208 degrees C, it was shown that whenever [ catalytic activity ] does not necessarily improve (Table 11). This observation was checked by the catalyst of 10 % of the weight of Mn, example 44E (149 degrees C), and example 44G (208 degrees C). Although these two examples had remarkably different distribution and it was high 30% at example 44E, the engine performance of an electrode catalyst was the same. Explanation of gap from the correlation of this high distribution-quantity activity is O. It can see with the XPS spectrum for 1s.

[0315]

If KMnO<sub>4</sub> concentration in the precursor solution of example 44E becomes high, it is clear from this XPS data to have the effectiveness which oxidizes the surfactant which exists in a solution. O about the surfactant (533.2eV) of example 44E The specific strength of 1s peak is far low compared with example 44D. Therefore, even if conversion temperature is quite low (149 degrees C), the burnout of a surface active agent is very effective. Clearly, if a surfactant still exists in a catalyst front face, it intercepts an active center, and even if MnOx distribution is appropriate, activity will become lower than example 44D. Furthermore, it is O of example 47D. O about a surfactant if the surfactant added as compared with 1sXPS spectrum is removed completely The reinforcement of a peak becomes still lower for 1s.

[0316]

If concentration of the surfactant in a precursor solution is made low, the effectiveness which is not good for MnOx cluster distribution will be done (compare example 30C with example 47D). However, if a surfactant exists, it will act as catalyst poison, distribution is more important for the instructiveness of there being few the amounts than a low thing, and whenever [ catalytic activity / which is acquired as a result ] is the same. Therefore, the amount of the surfactant of the amount of macromolecules should be made min in the suspension of a precursor.

[0317]

Example 44E prepared by spraying nozzle generation has the high engine performance equivalent to example

23A generated ultrasonically. Example 44E was 149 degrees C in the minimum conversion temperature, added the minimum surfactant and prepared it at 10 % of the weight of Mn, and 5 % of the weight of solution concentration. It seems that sufficient reaction rate which MnOx active species is formed in up to carbon support, and is distributed also on these special conditions (other conditions, such as the residence time) is secured.

[0318]

Compared with the carbon support used for the former spraying conversion sample (surface area 254m<sup>2</sup>/g), the bigger carbon support of surface area offers a big support front face rather than it can use for MnOx absorption. Contraction of the surface area after the spraying conversion observed by former carbon support is about 10 times as many order as this. By contraction of the surface area, since there was not sufficient surface area which raises distribution of MnOx of the amount of additions, even if it made [ many ] support of MnOx, it did not become useful for the activity of an electrode catalyst. Therefore, the carbon support with more large surface area from which porosity differs was chosen, and support of MnOx was large and examined whether it would be applicable to generation of the high electrode catalyst of distribution of an activity MnOx kind.

[0319]

The electrode catalyst example of this result is described in Table 12. Since viscosity was quite high, the KETJENBLACK (trademark) sample was thinned with water until carbon concentration decreased to 2% of the weight. Since viscosity was lower, the BLACKPEARLS (trademark) sample was thinned with water so that carbon might become 4% of the weight of concentration. The Mn/C ratio added KMnO<sub>4</sub> first dissolved in the water used for dilution of a sample to the sample higher than 10%. All the samples were processed changing an inlet temperature and the content of KMnO<sub>4</sub>.

[Table 12]

表 1 2 . 高表面積カーボン電極触媒の実施例

実施例	カーボンブラック源	Mn (wt. %)	入口温度 T (°C)	重量 (g)	回収率 (%)
35A	KETJENBLACK (R)	10	208	400	82
35B	KETJENBLACK (R)	10	315	440	88
36A	KETJENBLACK (R)	15	208	530	94
36B	KETJENBLACK (R)	15	315	510	92
37A	KETJENBLACK (R)	20	208	600	93
37B	KETJENBLACK (R)	20	315	660	94
38A	BLACKPEARLS (R)	10	208	490	98
38B	BLACKPEARLS (R)	10	315	500	99
39A	BLACKPEARLS (R)	15	208	570	97
39B	BLACKPEARLS (R)	15	315	570	98
40A	BLACKPEARLS (R)	20	208	610	96
40B	BLACKPEARLS (R)	20	315	630	98

The example was processed in the concurrent (co-current) spray drier in the sequence indicated to Table 12. The pressure of carrier gas is 5.63kg/cm<sup>2</sup> (80psi), and the carbon suspended solid was sent to the spraying nozzle the rate for 150-250ml/.

[0320]

Both carbon ingredients with large surface area distributed well, and MnOx obtained the electrode catalyst powder of large surface area. Drawing 37 and 38 express the dependency of the surface area to the amount of Mn adhering to carbon. When changing Mn concentration at 10 - 20 % of the weight, the catalyst which used carbon support of both types of BET surface area of 850-600m<sup>2</sup>/g as the base was acquired. Conversion temperature did not have big effect on surface area. In all cases, there is linearity clear to a dependency, MnOx is equally distributed over a carbon carrier surface, and this is interpreted as what brings about an additional coagulum and the additional condensation effectiveness.

[Table 13]

表 13. 高表面積カーボンブラックに基づいたサンプルの XPS データ

実施例	噴霧乾燥機入口温度 (°C)	Mn (wt. %)	Mn2p <sub>3/2</sub> 結合エネルギー (eV)	I (Mn 2p) / I (C 1s) (実験値)
35A	208	10	l. r. *	0.052
35B	315	10	641.6	0.143
36A	208	15	642.8	0.229
36B	315	15	644.1	0.257
37A	208	20	l. r. *	0.061
37B	315	20	643.2	0.330
38A	208	10	644.5	0.052
38	315	10	l. r. *	0.000
39A	208	15	643.1	0.269
39B	315	15	642.6	0.141
40A	208	20	n. a.	n. a.
40B	315	20	642.2	0.244

\* l. r. - 低溶解度

Drawing 39 and drawing 40 compare distribution (based on change of XPS I(Mn) I [ / ] (C) specific strength) of a MnOx kind as a function of support of Mn to KETJENBLACK (trademark) support ( drawing 39 ) and BLACKPEARLS (trademark) support ( drawing 40 ), and the inlet temperature of a spray drier. Since the surface area of a sample also changes as support of active species, and a function of a conversion inlet temperature, the exact comparison of distribution needs to apply KERUKUHOFU (Kerkhof) and Maureen's (Moulijn) XPS model. However, for evaluating distribution of the mol follow G and the activity phase of a catalyst first, it is XPS. I(Mn) I [ / ] (C) specific strength can be used.

[0321]

At both catalyst support, it is XPS to Mn content in 315 degrees C of inlet temperatures. The sample which I (Mn) I [ / ] (C) specific strength increases linearly is generated. At 208 degrees C of inlet temperatures, the results of two kinds of samples differ very much. Although the XPS value of 208 degrees C of inlet temperatures is lower than 315 degrees C in KETJENBLACK (trademark) support, on the other hand, it is quite high in BLACKPEARLS (trademark) support. These results have suggested having a role to formation and those distribution of active species with big chemical reaction of carbon support and mol follow G. It is Mn which supports this judgment. It is XPS data of the location (Table 12) of 2p<sub>3/2</sub> binding energy. Binding energy is the same as that of it of Mn (IV) oxidation state only with a small number of sample in emergencies, such as Examples 40B, 39B, and 36A. In example 35B, it has a value with quite high near and other samples on the other hand in Mn (III) oxidation state. Probably, these high values originate in whether the precursor which is not changed exists or the kind from which MnOx higher than Mn (IV) oxidation state was changed exists.

[0322]

Two additional groups of a MnOx/C electrode catalyst were prepared using the spray drier. The sample shown in Table 14 is what carried out spray drying using the average flow spray drier, and the sample shown in Table 15 was generated using the interflow spray drier. Generally, although the outlet temperature of a concurrent spray drier was restricted to about 200 degrees C, this is a maximum temperature to which a particle is put. in a mixed spray drier, a particle is longer -- still higher rise temperature is experienced as time amount stagnation is carried out and they move toward an introductory gas stream (an inlet temperature is more remarkably [ than outlet temperature ] high). By using the configuration of two different spray driers, the effectiveness of the career of the time amount/temperature exerted on the property and the electrochemical engine performance of a MnOx/C electrode catalyst was able to be compared.

[Table 14]

表 14. 並流噴霧乾燥機でスプレー乾燥された電極触媒

サンプル	Mn (wt. %)	カーボン支持体	入口温度 (° F)	生産率 (g/hr)
105A	10%, 1% Ag	SHAWINIGAN BLACK (R)	400	590
103B	10% Mn	SHAWINIGAN BLACK (R)	400	560
104A	10% Mn	SHAWINIGAN BLACK (R)	600	700
103A	5% Mn	SHAWINIGAN BLACK (R)	400	570
103C	5% Mn	SHAWINIGAN BLACK (R)	600	680
104B	15% Mn	SHAWINIGAN BLACK (R)	600	560
104C	20% Mn	SHAWINIGAN BLACK (R)	600	648
106A	10%, 1% Ag	グラファイト化 VULCAN (R)	400	300
106B	10%, 1% Ag	グラファイト化 VULCAN (R)	600	260
105B	10% Mn	グラファイト化 VULCAN (R)	400	225
105C	10% Mn	グラファイト化 VULCAN (R)	600	195
108A	10%, 1% Ag	ノリット	400	900
108B	10%, 1% Ag	ノリット	600	600
106C	10% Mn	ノリット	400	200
114C	10% Mn	PWA	600	517
107B	10%, 1% Ag	PWA	400	975
107C	10%, 1% Ag	PWA	600	200
107A	10% Mn	PWA	400	700
115A	10% Mn	PWA	600	210
19A	10% Mn	PWA	400	-

As shown in Table 14, in order to generate the MnOx/C electrode catalyst which returns oxygen, the carbon support from which many differ was used. Different carbon support offers an advantage which is different for the engine performance and application in a special application of these catalysts from which the cell for hearing aid to high power cells, such as a pocket device, change. Each of the carbon support to be used has different initial surface area, and is SHAWINIGAN. The range of 80m<sup>2</sup>/g to 1400m<sup>2</sup>/g of BLACKPEARLS (trademark) and KETJENBLACK (trademark) of BLACK (trademark) is reached. Furthermore, the carbon particle size of the beginning of such support in the suspended solid used for spray drying differs greatly, and is SHAWINIGAN. For BLACK (trademark), 55nm, BLACKPEARLS (trademark), and KETJENBLACK (trademark) are 400nm and norit. SA-3 and PWA are 22 microns.

[0323]

That the electrode catalyst which used all support of these various mol follow G as the base can be generated expresses the flexibility of the spray drying generating method for dealing with various support, and the

versatility of the catalyst method of preparation.

[Table 15]

表 15. 混合流噴霧乾燥機でスプレー乾燥された電極触媒

サンプル	組成	カーボン 支持体	入口温度 (° F)	生産率 (g/hr)	表面積 (m <sup>2</sup> /g)
135A	10% MnO <sub>2</sub>	PWA	400	276	300
135B	5% MnO <sub>2</sub>	PWA	400	645	386
135C	10% MnO <sub>2</sub>	PWA	375	639	455
136A	5% MnO <sub>2</sub>	PWA	375	501	490
136B	10% MnO <sub>2</sub>	PWA	350	675	400
136C	5% MnO <sub>2</sub>	PWA	350	780	380
137A	10% MnO <sub>2</sub>	PWA	300	648	380
137B	5% MnO <sub>2</sub>	PWA	300	324	370
161A	10% MnO <sub>2</sub>	PWA	375	-	220
161B	10% MnO <sub>2</sub>	PWA	300	-	300

Electrochemical evaluation of a MnOx/C catalyst was also carried out. The electrode consisted of catalysts of 20 mg/cm<sup>2</sup> using the gaseous diffusion layer which consists of XC-35 of 50 mg/cm<sup>2</sup>. With the 7-N KOH electrolytic solution and air, the current collector of a nickel mesh was used at atmospheric pressure and a room temperature.

[0324]

Drawing 41 and drawing 42 show what the electrochemical activity of these carbon does not change even if BET surface area decreases (within the limits of the experimental error). This is considered that the electrochemical reaction which does not use internal porous space occurred by the reason of whether internal porous space is blockaded by the big MnOx coagulum or internal porous space did not contact MnOx from the beginning. Furthermore, even if there were these parameters, it is shown that there is little temperature dependence. Although the surface area of a catalyst influences the limitation of diffusion, it is important to understand that it should have effect for the engine performance of a catalyst with the specific big surface area of active species.

[0325]

This electrochemical test result is [ drawing 43 / catalyst / on KETJENBLACK (trademark) carbon support / electrode ] SHAWINIGAN to drawing 45 about the electrode catalyst on BLACKPEARLS (trademark) carbon support in drawing 44 . It is plotting about the sample chosen from on MLACK support, norit support, and PWA carbon support. It is shown that the sample which has electrochemistry activity which is different on the same spray drying conditions in respect of others generates the result according to the concentration of active species and the class of support. The electrochemical thing that has the good engine performance is sample 37A set in the low current range among the sample of a single string on KETJENBLACK (trademark) support, and it is sample 35B in the high current range ( drawing 43 ). The electrochemical thing that has the good engine performance is sample 40B in the low current range among the sample of a single string on BLACKPEARLS (trademark) carbon support, and it is sample 40A in the high current range ( drawing 43 ). For the data shown in drawing 45 , the electrode catalyst supported on norit carbon and PWA carbon is SHAWINIGAN. Compared with the electrode catalyst supported on MLACK, it means having electrochemical higher activity by the reason the surface area of the former support is probably larger.

[0326]

The experiment about mixed spray drying (Table 15) focused on preparation of the MnOx/C electrode catalyst on PWA carbon support. It is shown that surface area becomes max and the plot of the surface area of the MnOx/PWA catalyst prepared by the interflow spray drying of drawing 46 subsequently decreases rapidly in the place beyond a certain critical temperature. Both catalysts which supported MnOx have the same surface area until they reach max at 191 degrees C (375 degrees F). Once it passes over the critical temperature of 191 degrees C (375 degrees F), also in which support, surface area will be lost greatly. Although the way of the catalyst of 10 % of the weight of MnOx(es) has large disappearance surface area, this will be because

condensation of a surface kind is proportional to concentration. If a metallic oxide increases to a front face, distribution will decrease, and the big coagulum which blockades internal porous space is formed.

[0327]

Many factors affect the electrochemical activity of the supported MnOx catalyst. All the concentration of spraying conversion conditions, a surface active agent, carbon support, and a precursor does effect strong against the engine performance of an electrode catalyst.

[0328]

As it saw in the front MnOx catalyst, there is no direct relation between the surface area of a catalyst and electrochemical activity. As shown in drawing 47, change with a potential of 10mA is not large. When surface area decreases to 150m<sup>2</sup>/g by the temperature rise, the 10mA potential difference is only 30mV. It has suggested that these results have the factor which should take many into consideration more. moreover, a hole which is different from different surface area since it does not depend for electrochemical activity on the surface area of a catalyst greatly -- the catalyst which has distribution of size is a important matter with the ability of a different advantage to also be offered [ important ], in order to make into min the diffusion limitation in the inside of the device which is working.

[0329]

The data shown in drawing 48 and drawing 49 show the slight difference of the electrochemical engine performance between samples. The comparison of the engine performance under air and pure oxygen offers the information about diffusion of the gas in an electrode, and an ionicity kind, and the property of migration. The diffusibility and migratory ability of a layer which supported the predetermined ingredient are so good that there are few differences during the plot of oxygen and air as compared with an external standard ingredient. Therefore, a strong interaction is between support of the metallic-oxide kind on the thickness of a layer, and a carbon carrier surface. In order to obtain the greatest engine performance in kinetics, many active sites are important (shown by the TAFERU Fig. of drawing 49). However, it can become harmful to the engine performance of a layer to add much more electrode catalysts, since the grand total of an active site is increased if the electrode catalyst powder which has the optimal quantity of an active site per unit mass of an electrode catalyst is taken into consideration (for the thickness of a layer to increase) under the conditions to which the engine performance is restricted by ionicity and/or a firedamp migration ohmic with high current density.

[0330]

Based on these data, the catalyst samples 135C and 137C were chosen, and in order to carry out the preliminary test of the zinc air battery for hearing aid, it expanded to the batch of a 4kg trial scale. Drawing 50 and drawing 51 are measuring the electrochemical activity of a trial scale batch with the first sample operation. The electrochemical activity of sample 161A (expansion of sample 135C) did not have repeatability like sample 161B (expansion of sample 137A). The surface area of these two catalysts is the cause. Although, as for surface area, there is no direct relation to electrochemical activity, it may have suggested the potential problem, so that some opinions may see. Rather than an experiment batch, for a scale factor 2, the surface area of catalyst sample 161A is small, and is experienced before, and reliance also has a big difference. As for the particle size distribution of a real \*\*\*\*\* batch, the particle shows that it is almost twice as many size as this rather than Samples 135C and 137A. By the further investigation, it became clear that the airstream of two hydraulic nozzles had decreased about 10%. Since big shearing force generates a globule rather than it is based on the high-speed gas in two hydraulic nozzles, this is explanation which has validity most.

[0331]

In the case of the gas diffusion electrode for a metal-air cell or a fuel cell, a barrier layer is responsible for the catalytic reaction of gas, and opts also for the engine performance of a power unit. The barrier layer is close to a hydrophobic layer. A hydrophobic layer helps the firedamp migration to a catalytic site, and an electrolyte prevents what "is oozed" (weeping) from a device, preventing to coincidence that external moisture makes a power unit out of balance. Hydrophobicity is controllable by the hydrophobic layer which has a single hydrophobic layer or an inclination in power unit structure. In many cases, a barrier layer consists of mixture of the carbon black which carried out TEFLON(ing) (trademark) or Teflon (TEFRON) processing with the catalyst. A hydrophobic layer can be replaced with the component which helps migration of a kind required for catalytic reaction. For example, as for a barrier layer, in a PEM fuel cell, it is possible for it to be the catalyst which coexists with NAFION (trademark). A barrier layer works as the transition section between a



hydrophobic layer and an electrolyte. The most important technical problems concerning adhesion of a barrier layer are maintaining the activity of the catalyst in a barrier layer, having the optimal presentation of hydrophobicity / migration assistance, and a catalyst component, and preparing the formula of a right medium / configuration which should adhere. The attainment to the thickness of this layer and the catalytic site of gas and the controlled hydrophobicity opt for the engine performance of a power unit.

[0332]

It depends for the adhesion technique of a barrier layer on the structure of a catalyst particle and a hydrophobic component, and mol follow G. The quantum regurgitation according [ size ] to a syringe is more suitable for the particle size of less than about 25 microns, and techniques, such as screen-stencil or spreading by wire-coater, are more suitable to a particle with a size of about 25 microns or more. An adhesion technique determines the presentation of a formula further. For example, isopropanol is not suitable for the quantum regurgitation by the syringe for the hypoviscosity and high vapor pressure.

[0333]

The example of the pharmaceutical preparation for the syringe quantum regurgitation was generated as follows. The metal oxide catalyst was mixed with TEFRON (trademark) powder to the weight ratio of 5:1, and, subsequently to the inside of an alpha-terpineol, it distributed. The barrier layer consisted of 20 - 40% of the weight of solid content. The pharmaceutical preparation containing the metallic oxide mixed with the Teflon processing black which it was similarly supported on carbon and was distributed in isopropanol for screen-stencil was prepared. The amount of solid content support of this pharmaceutical preparation was changed to 10 - 40% of the weight.

[0334]

The thickness of a layer is controllable by solid content support of the activity ingredient of an ink formula, and the writing speed in the quantum regurgitation. The inclination under layer presentation is controllable by the number of the presentation of ink, writing speed, and the adhering substrate layers.

[0335]

With the direction for use of a catalyst, distribution, and a presentation, although the reaction rate of an electrode is controllable, it originates mainly in the thickness of a layer, the presentation of a layer, and the porosity of a layer, and a limit and a migratory limit of the electric resistance of a power unit produce it. The thickness of a layer is controllable by changing the powdered weight and the powdered adhesion approach which are supported in a layer. The presentation of the adhesion approach and a layer determines the ease of reaching to the porosity and the catalyst bed of a layer on the other hand. When these ingredients are printed, there is also an advantage which can print support of a barrier layer from the small quantity of 2 mg/cm<sup>2</sup> to the large quantity of 20 mg/cm<sup>2</sup>. The range of this barrier layer support demonstrates dramatic effectiveness in a different engine-performance field.

[0336]

It depends on the volume of a different layer, therefore the thickness of various layers for the energy density obtained by the power unit. The volume density obtained from a power unit is so high that a layer is thin. Some examples of the film printed for metal-air cells are described below. <BR> [0337]

In order to control a migration process, the formula of the ink containing an electrode catalyst and other hydrophobic powder was produced, and it adhered on the current collector front face of the silver printed for the purpose of making the film of this ingredient. The circumference of an edge of the barrier layer adhering to a current collector substrate was observed. The appearance of an edge expressed the characteristic mol follow G of a particle clearly, and the thickness of a layer was the thickness of about 1 particle.

[0338]

As a result of being able to determine the relation of the optimal structure-engine performance quickly, a perfect gas electrode can be manufactured by this invention. This gas diffusion electrode consists of a gaseous diffusion layer of the porosity which printed the silver current collector on it. A current collector's dimension is 300 microns in the line breadth of 40 microns, height of 15 microns, and spacing. The barrier layer which adhered on the current collector / gaseous diffusion layer consists of an ingredient catalyzed in chemistry conversion of gas, and an ingredient which controls hydrophobing of this layer. This layer is about 30 microns in thickness.

[0339]

The property of the electrochemical engine performance of a layer which carried out direct writing can be

quantified by the polarization curve. The polarization curve of various different layers using the same ingredient in the case of the air electrode under alkali conditions is shown in drawing 52. A continuous line is polarization data measured in oxygen, and a dotted line is polarization data measured in air. The structure which supported the barrier layer of 20 mg/cm<sup>2</sup> adhered using the technique which is not in which the layer of little support (thin) of the conventional approach should adhere. By the quantum regurgitation direct writing by the syringe, other barrier layers adhered the amount of support from which a single string differs. the amount of direct writing support from which 5 mg/cm<sup>2</sup> in the inside of air and 12 mg/cm<sup>2</sup> differ has the engine performance lower than the layer of 20 mg/cm<sup>2</sup> which has the same engine performance mutually, was alike as usual, and adhered. This is being able to expect from an activity ingredient not recognizing little deer existence. However, since, as for the direct writing layer of 5 mg/cm<sup>2</sup>, the structure of the use property of migration and a catalyst of a layer is improving in air, compared with the conventional adhesion layer which has the ingredient which is 4 times, the engine performance in air is only slightly low. Therefore, in the air which is useful gas practical, the engine performance of these two layers is equivalent. A difference (in practice measurement of an oxygen density dependency) of the electrochemical engine performance in the antiaircraft mind in oxygen clarifies the diffusion property of a layer. As these examples show, the data of the electrochemistry activity of a series of MnOx/C catalysts show that different conditions are need according to the carbon support used for the class of spray drier to be used, specific catalyst support, and preparation of an electrode catalyst, in order to gain the engine performance of the optimal electrode catalyst. This is based on the hysteresis of different temperature-time amount which an electrode catalyst particle experiences, and while the active species of distribution which is different, and a class processes it, it is generated. Since the expansion experimental result of a MnOx/PWA sample changes the activity surface kind which will be generated if conditions are different, in order to secure the repeatability of the electrochemical engine performance, it has suggested that it is necessary to control the parameter of spraying processing carefully. This is true especially when using high conversion temperature.

[0340]

2. NiCoOx bifunctional electrode catalyst The bifunctional electrode catalyst by reduction/emission of oxygen is a complicated electrochemistry catalyst system. Based on the fact that both oxygen emission and electric reduction of oxygen are irreversible reactions, these electrode catalysts must own the catalytic activity core of at least two different classes. It chose from some possible chemicals for evaluation of mixed oxide system NiO:CoO (1:2). This is the least complicated bifunctional electrode catalyst, and shows exceptional activity and sufficient cycle life.

[0341]

The cycle life of a bifunctional electrode catalyst is restricted by destruction of the carbon support under oxygen emission (cel charge), and is called "electrochemical combustion" of carbon. Graphite carbon has resistance in the electrochemical oxidation under oxygen emission rather than amorphous carbon. A NiO:CoO complex electrode catalyst is usually acquired by the precipitate on conventional activated carbon. It was used in order to compare with this invention the catalyst made by this approach.

[0342]

The example was prepared in order to show this invention about a self-support bifunctional electrode catalyst. The engine performance of these catalysts was evaluated about the period of whenever [ catalytic activity ], and an electrode. The conventional method of preparing a gas diffusion electrode depends a catalyst bed on making it combine with acetylene carbon. In the following examples, the electrode was prepared without using carbon entirely. Carbon was transposed to TEFRON (trademark) powder as a binder.

[0343]

The catalyst of the following examples was prepared using the ultrasonic aerosol generation machine. The precursor solutions used in order to manufacture a catalyst are nickel(NO<sub>3</sub>) 26H<sub>2</sub>O (nickel nitrate) and Co (NO<sub>3</sub>) 26H<sub>2</sub>O (cobalt nitrate), and the ratio of NiO:CoO was set to 1:2.

[0344]

It is GURAHU about the catalyst on carbon support. It prepared with the 1300 distribution object using the precursor of nickel and cobalt. It is GURAHU in order to prepare 10 - 20% of the weight of NiO-CoO on carbon. 1300 solutions were thinned with water, and it mixed with nickel oxide and a cobalt oxide precursor so that the solid content in a solution might become 5 % of the weight. The catalyst particle which processed these precursor solutions at 300 degrees C or 400 degrees C, and was supported was generated.

[0345]

The same nickel and the cobalt precursor which were diluted with deionized water were used for the self-support catalyst. Subsequently ultrasonic generating of these solutions was carried out using the transducer, and it processed at the temperature of the range of 400 degrees C - 600 degrees C.

[0346]

\*\*\*\* (Ag) was introduced into some catalyst particles in order to raise the conductivity of a catalyst. It is known that silver will work as an accelerator in a catalyst formula again. The silver content of a catalyst formula was changed at 1 - 80 % of the weight.

[0347]

In electrochemical evaluation of a NiO:CoO bifunctional electrode catalyst, it included in asking the beginning for the polarization curve in the inside of the electrolyte for screening, and the lab functional test cel which uses MH anode plate in order to actually carry out MH-air system and to examine a cycle life. The electrode was prepared using the conventional dry type powder compression technology from the catalyst sample. An electrode consists of a gaseous diffusion layer and a barrier layer. A gaseous diffusion layer consists of black in which 50 mg/cm<sup>2</sup> pressed at 300kg/cm<sup>2</sup> and 300 degrees C in the mold groove of 2 10cm carried out Teflon processing. A barrier layer consists of mixture of 10 mg/cm<sup>2</sup> which mixed Teflon processing carbon with the bifunctional electrode catalyst by the ratio of 3:1. The gaseous diffusion layer and the barrier layer were pressed at the elevated temperature by 300kg/cm<sup>2</sup> on nickel mesh. Electrochemical measurement was a thing about the polarization behavior of the beginning of a bifunctional electrode. The trial was performed in 31% of the weight of the aqueous KOH solution at the room temperature. The zinc line which carried out installation soon was used for the front face of an air electrode of operation as a Zn/ZnO reference electrode.

[0348]

Table 16 summarizes the catalyst produced using the spraying pyrolysis technique. In Table 16, the peak which was in agreement with the surface area, the particle size (d<sub>90</sub>), and the XRD technique of a different catalyst sample is listed.

[Table 16]

表 16. NiO-CoO 触媒の要約

サンプル	組成	温度 (°C) /流量 (lpm)	表面積 (m <sup>2</sup> /g)	XRD のピーク	PSD d <sub>90</sub> (μm)
056064A	10%NiCoO <sub>x</sub> /カーボン	300/5	27.0	NiCo <sub>2</sub> O <sub>4</sub>	2
087064B	20%NiCoO <sub>x</sub> /カーボン	300/5	42.0	NiCo <sub>2</sub> O <sub>4</sub>	2
056066B	NiCoO <sub>x</sub>	400/5	3.0	NiCo <sub>2</sub> O <sub>4</sub>	11.4
056067A	20%NiCoO <sub>x</sub> /カーボン	300/5	31.0	NiCo <sub>2</sub> O <sub>4</sub>	3.0
056067B	20%NiCoO <sub>x</sub> /カーボン	400/5	36.0	NiCo <sub>2</sub> O <sub>4</sub>	2.7
105006A	NiCoO <sub>x</sub>	400/5	4.9	NiCo <sub>2</sub> O <sub>4</sub>	11.6
105006B	NiCoO <sub>x</sub>	500/5	9.7	NiCo <sub>2</sub> O <sub>4</sub>	7.5
105006C	NiCoO <sub>x</sub>	600/5	10.7	NiCo <sub>2</sub> O <sub>4</sub> , NiO	4.0
109022A	NiCoO <sub>x</sub>	500/5	24.2	NiCo <sub>2</sub> O <sub>4</sub>	-
109022B	NiCoO <sub>x</sub>	600/5	11.5	NiCo <sub>2</sub> O <sub>4</sub>	-
109028A	NiCoO <sub>x</sub>	600/45	29.3	NiCo <sub>2</sub> O <sub>4</sub>	4.8
109035A	1%Ag/NiCoO <sub>x</sub>	800/45	7.0	NiCo <sub>2</sub> O <sub>4</sub> , Ag, CoNiO <sub>2</sub>	5.2
109031A	10%Ag/NiCoO <sub>x</sub>	800/45	6.5	NiCo <sub>2</sub> O <sub>4</sub> , Ag, CoNiO <sub>2</sub>	4.7
109032A	50%Ag/NiCoO <sub>x</sub>	800/45	2.9	NiCo <sub>2</sub> O <sub>4</sub> , Ag, CoNiO <sub>2</sub>	5.5
109033A	80%Ag/NiCoO <sub>x</sub>	800/45	2.4	NiCo <sub>2</sub> O <sub>4</sub> , Ag	3.4
056107A	NiCoO <sub>x</sub>	600/45	28.8	NiCo <sub>2</sub> O <sub>4</sub>	5.4
056108A	NiCoO <sub>x</sub>	675/45	17.8	NiCo <sub>2</sub> O <sub>4</sub>	5.3
056109A	NiCoO <sub>x</sub>	750/45	11.9	NiCo <sub>2</sub> O <sub>4</sub>	5.5
056110A	NiCoO <sub>x</sub>	600/20	23.6	NiCo <sub>2</sub> O <sub>4</sub> , NiO	4.9

Samples 056064A, 087064B, 056067A, and 056067B were catalysts currently altogether supported on carbon. Sample 056066A was the self-support catalyst prepared on the same unit. The electrode was prepared with the self-support bifunctional catalyst, the electrode catalyst supported on carbon black, and the standard catalyst made in the conventional precipitate procedure. Drawing 53 shows the polarization curve of a test electrode. A dotted line shows the polarization curve of the electrode made from the catalyst of the conventional advanced technology. It is found that the self-support electrode catalyst prepared by this invention shows the most advantageous engine performance in oxygen reduction. The predominance of the same electrode catalyst is clear also in oxygen release reaction, as shown in drawing 54. In this case, the NiO:CoO electrode catalyst of this invention makes an oxygen molecule emit with the lowest anode potential.

[0349]

What re-calculated this result about the ratio (it expresses with percent) of the cathode/plate voltage in predetermined current density is shown in drawing 55. Drawing 55 expresses the dynamic electricity effectiveness (voltaic efficiency) of the bifunctional oxygen electrode concerning the energy loss in charge/discharge cycle of a cel directly.

[0350]

The dynamic electricity effectiveness of the electrode made from this catalyst with the engine performance which was excellent in the NiO:CoO electrode catalyst of this invention in both an oxygen reduction reaction and oxygen release reaction is the highest, and is [ cm / in / 10-20mA // the anticipation operating current consistency range of 2 ] for 65 to 62%. The dynamic electricity effectiveness exceeding 55% is practical, and since it does not usually exceed 60% in a commercial cell system, this is very promising.

[0351]

Based on the screening result of this half-cel polarization, the experiment with a non-supporting bifunctional electrode catalyst was further conducted in the lab MH-air cel.

Samples 105006A-105006C were made from the elevated temperature to the unit of a laboratory scale. The surface area of a catalyst was increased by raising the spray drying temperature of a catalyst. It was shown that the XRD spectrum of these catalyst samples exists in catalyst 105006C which a different phase, i.e., a NiO phase, made from 600 degrees C.

[0352]

The electrode was made from the catalyst as mentioned above, and the polarization curve was measured. The TAFERU Fig. was plotted about three catalysts. A TAFERU Fig. is the graph of the logarithm (unit mA/cm<sup>2</sup>) of delta E (unit mV) opposite current density. Delta E is the difference of the electrode potential measured in air and oxygen. The plot inclination of sample 105006C is the smallest as compared with the inclination of other two catalysts, and means that this is a better catalyst so that it may see from the TAFERU Fig. of drawing 56. However, it is not clear whether it is what is depended on existence of whether it being what the low inclination of catalyst 105006C depends on big surface area, and a new NiO phase.

[0353]

Big surface area can explain that the way of 105006B is the good engine performance from 105006A from that of a 105006B catalyst.

As mentioned above, some Ag was included in Catalysts 109033A-109035A. Ag content was changed at 1 % of the weight - 80 % of the weight, and spray drying of the precursor solution was carried out at 800 degrees C. The SEM photograph of a different catalyst containing these Ag did not show a difference at all to the structure of these catalysts. However, the BET surface area of a catalyst particle decreased sharply to about 2m<sup>2</sup>/[ of 80 % of the weight (109033A) of 29(109028A) m<sup>2</sup>/g to Ag which does not contain Ag ] g. XPS evaluation showed that the nickel:Co ratio of catalyst 109028A was 35:65. As for the ratio of nickel:Co:Ag in catalyst 109031A and 109032A, it was detected by XPS that it is 35:61:1 and 45:52:3, respectively.

[0354]

The polarization curve of the catalyst which doped these Ag is shown in drawing 57. Although catalyst 109032A showed the best engine performance electrochemically, all the polarization curves of a catalyst are hard to be referred to as that Ag phase brings about the difference in the engine performance in a bifunctional catalyst conclusively so that it may be mutually near. However, the catalyst which doped these Ag was prepared using the same quantity of the catalyst. Therefore, reduction of oxygen and the active site for emission would be inadequate.

[0355]

It is a bigger manufacture unit, and the catalyst samples 056107A, 056108A, and 056109A changed temperature, kept the presentation of a precursor solution constant, they kept constant the rate of flow of carrier gas (air), and manufactured it. If an operating temperature is raised from 056107A to 056109A, the surface area of the particle measured with the nitrogen adsorption process will decrease. As the electrochemical engine performance is also shown in drawing 58, it decreases in the direction where surface area decreases. That surface area is large means that a catalyst is [ many / therefore / exposure of a catalytic site ] the better engine performance.

[0356]

From the TAFERU Fig. of the electrode shown in drawing 59, catalyst 056110A shows the best electrochemical engine performance. Catalyst sample 056110A is the same temperature as 056107A, however was manufactured by the 25lpm low carrier gas style. Although the surface area of catalyst 056110A was close to it of 056107A, the engine performance of this catalyst was more good. Since the operation rate of flow which produces 056110A was the one half of that of 056107A, the catalyst particle produced by the low rate of flow passed through the long residence time. When the residence time is more long, a catalyst comes to have a crystalline substance phase which becomes a crystalline substance more or is different compared with 056107A.

[0357]

In order to investigate this thing, the XRD plot of these two catalysts was compared that it should be determined whether crystallinity had a difference. The nickel oxide (NiO) phase existed from the XRD spectrum of catalyst 056110A. The nickel oxide (NiO) phase did not exist in catalyst 056107A. By existence of the crystalline substance phase of nickel oxide, 105006C was the best catalyst. Therefore, catalyst 56110A was chosen as the best self-support bifunctional catalyst for the further electrochemical trial.

[0358]

The main problems which restrict the cycle of a gas electrode as argued above are combustion of a carbon component. The self-support catalyst which has the good catalyst engine performance is the 1st process which removes carbon from an electrode. The conventional method of preparing a gas diffusion electrode is combining a catalyst bed with acetylene black. It experimented and it was seen whether influence the engine performance of a half-cel. Association of a barrier layer added and attained [ 1st ] the acetylene black (35 % of the weight) which is expressed with AB35T and which carried out Teflon processing. In the 2nd electrode, association of a barrier layer was carried out by mixing in the pure TEFRON (trademark) powder expressed with PTFE. Although both cases used the same electrode catalyst, i.e., sample 056110A, the only difference was that the 2nd electrode does not contain carbon.

[0359]

Drawing 60 is the polarization curve of oxygen reduction of two electrodes and emission. When PTFE is [ current density ] two or more 20 mA/cm in the binder of a barrier layer so that drawing 60 may see, there is a limitation of clear gas migration in an oxygen reduction field. Emission of oxygen is not influenced [ remarkable ] by change of a binder. It is checked that the gaseous diffusion limitation of a PTFE electrode makes it lower effectiveness with the dynamic electricity effectiveness drawn from former polarization data as compared with AB35T electrode shown in drawing 60.

[0360]

They were chosen as cycle life test even if diffusion of a PTFE type oxygen electrode was inadequate. Cycle operation of the electrode in the half-cel in charge / discharge current 10 mA/cm<sup>2</sup> showed that a system deteriorated in 30 - 35 cycle. This process returned, after replacing the electrolyte. Dark-brown coloring was observed by the consumed electrolyte and analysis of the consumed electrolyte showed existence of carbon to it. Partial oxidation of the carbon ingredient used into the gaseous diffusion layer has caused contamination of this electrode.

[0361]

Cycle operation of the electrode was carried out by charge/discharge current of 5 mA/cm<sup>2</sup> at the pan. Since many cycle period electrolytes were not changed, the result of the carbon contamination in an electrolyte is not clear. The fall of current density helps the increment in the cycle life of an electrode.

[0362]

The result of electrode degradation under cycle operation was studied using the polarization curve of the oxygen reduction obtained 100 cycles [ of the electrode prepared newly and the same electrode ] after, and emission. The overall fall of whenever [ catalytic activity / of oxygen reduction and both emission ] can be seen detected to drawing 62 after cycle operation.

[0363]

Cycle Volta METORI (voltametry) was examined and the cause of a fall of the overall activity regularly detected by polarization measurement was evaluated. drawing 63 -- electrode [ before cycle operation ] (chain line); -- the same electrode after 100 cycles after (dotted line); 100 cycle shows the cycle voltamogram (voltamograms) of; in a new electrolyte in the used electrolyte.

[0364]

The peak of a voltamogram is equivalent to the transition state of the reduction/oxidation from which oxygen becomes absent into a catalyst ingredient. They are related to whenever [ catalytic activity / of oxygen reduction and emission ]. The clear passive state effectiveness is looked at by the old electrolyte. This effectiveness is partially compensated by changing an electrolyte (it returns).

[0365]

The partial oxidation of the carbon from a gaseous diffusion layer can assume that it makes a brown product generate. The catalyst front face in a barrier layer continues being adsorbed, and they passivate a catalyst. Adsorption is partially reversible and some ingredients which blockade the catalyst are removed by changing an electrolyte.

[0366]

It is proved that a self-support nickel oxide cobalt catalyst can manufacture the above-mentioned example with the spraying processing technique of this invention. The catalyst showed good catalytic activity. The catalyst engine performance excellent in existence of the mixed oxide phase of big surface area and nickel, and cobalt is given. The short cycle life of a bifunctional air electrode is based on the corrosion of the electrode under oxygen emission. A carbon ingredient may be replaced with the carbon which has drag force in oxidization more if it takes into consideration that a gaseous diffusion layer is corroded in oxidization. Since the graphite of a high crystalline substance is resistant from carbon black to oxidization, the Teflon processing acetylene black (35 % of the weight) used for the gaseous diffusion layer can be transposed to Teflon processing graphite powder. Other corrections will be excluding carbon from an electrode completely using the gaseous diffusion layer from which a pure TEFRON (trademark's) sheet's etc. differs.

[0367]

### 3. Metal-Carbon Support Electrode Catalyst Particle [0368]

Other examples by this invention are prepared and this is shown in Table 17. The powder batch of an example was prepared by ultrasonic generation, and aerosol was heated in the tube furnace reactor. All examples are GURAHO. It prepared using 1300. Corresponding Pt precursor of an amount was dissolved in carbon suspension, and, in addition, the precursor was formed. Table 17 shows the class of Pt precursor to be used, carrier gas, conversion temperature, and the target nominal rating concentration of Pt in the inside of the last catalyst.

[Table 17]



表 17. 超音波で Pt/C パウダーの条件

実施例	Pt 前駆体	Pt (wt. %)	炉の温度(°C)	キャリアガス
P27B	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	400	空気
P31B	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	700	空気
P31C	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	500	空気
P32A	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	300	空気
P32B	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	200	空気
P33B	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	200	N <sub>2</sub>
P33C	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	300	N <sub>2</sub>
P36A	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	300	N <sub>2</sub>
P36B	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	300	N <sub>2</sub>
P36C	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	500	N <sub>2</sub>
P37A	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	500	N <sub>2</sub>
P37B	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	500	N <sub>2</sub>
P37C	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	700	N <sub>2</sub>
P37D	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	700	N <sub>2</sub>
P37E	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	700	N <sub>2</sub>
P38A	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	500	N <sub>2</sub>
P38B	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	500	空気
P39A	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	20	400	空気
P39B	H <sub>2</sub> Pt (OH) <sub>6</sub>	10	400	空気
P40C	H <sub>2</sub> Pt (OH) <sub>6</sub>	10	300	空気

TEM analysis had the spherical secondary carbon particle on parenchyma, and changing particle size between 1-2 micrometers was shown. An aggregated particle (support phase) consists of a primary carbon particle with a diameter of about 30 nanometers, a Pt particle of various particle size, and a particle cluster distributed there. A secondary electrode catalyst particle has porous structure in altitude.

[0369]

The surface area of the ultrasonic generation Pt/C catalyst powder by this invention was analyzed using the BET nitrogen adsorption process. A result is summarized to drawing 64 and shown. Both conversion temperature and a carrier gas presentation affected the surface area of a catalyst. When using air as carrier gas, surface area is more large at 300 degrees C (89m<sup>2</sup>/g) compared with the conversion temperature of 200 degrees C (22m<sup>2</sup>/g). However, even if it raised conversion temperature to 400 more degrees C, surface area did not change a lot. When by contrast using nitrogen as carrier gas, the surface area of a catalyst increased to 125m<sup>2</sup>/g at 500 degrees C, and when conversion temperature was further raised to 700 degrees C, \*\*\*\*\* decreased too.

[0370]

The next conclusion will be obtained if it analyzes as a function of spraying conversion temperature and a carrier gas presentation of change of surface area.

- When using air as carrier gas, the conversion temperature of 300 degrees C or more is not useful in order to expand surface area.

[0371]

- When using nitrogen as carrier gas, generally powdered surface area is large compared with the powder which generated air as carrier gas.

- If nitrogen is used as carrier gas, the conversion temperature of 500 degrees C is advantageous to manufacturing powder with large surface area.

[0372]

- The surface areas after spraying conversion are or less at least 1 of the original carbon support / 3.

In order to acquire the information about the distribution in the oxidation state of Pt, and a catalyst, XPS analysis of a sample was performed. The comparison between the samples which analyzed the three main properties of a XPS spectrum and generated them on different conditions was performed. Binding energy Pt

The location of 4f<sub>7/2</sub> photoelectron shows the oxidation state of Pt, and is;Pt. 4f pair C The specific strength of 1s photoelectron peak shows distribution of Pt, and is;N. The appearance and its C of 1s photoelectron peak The specific strength to a peak shows the level of an impurity, and the conversion degree of a platinum precursor for 1s.

[0373]

Record of all preparation conditions and spectrums and data processing are the same about all samples. In order to perform XPS analysis, it pressed in the indium foil (99.9%) from which the sample was beforehand washed in HNO<sub>3</sub>, and the surface impurity was removed, and prepared.

[0374]

the XPS spectrum of all catalysts -- AXIS HSi (Kratos Analytical) spectrometer -- pass energy 80eV --  $\Delta E$  -- it was fixed, and it was made to operate and recorded using the monochrome mate aluminum anode plate (aluminum K $\alpha$ =1486.7eV, 225W). The residual pressure of an analysis chamber was 1x10 to 9torr (1torr = 133.3Pa). It is C about the location of a peak. It calculated about 1s=284.6eV binding energy. The following XPS peaks, i.e., Pt, 4f, C 1s, O 1s and N 1s was expressed and recorded on electron level. Before obtaining the spectrum of high resolution, the scan for investigation was once carried out in the range of 75-1175eV binding energy. The reinforcement of an experimental value graduated, measured and calculated the original peak from the area of a corresponding peak. Pt The area of 4f peak is Pt. Both 4f<sub>7/2</sub> peak and 4f<sub>5/2</sub> peak are included. A result is shown in Table 18.

[0375]

As listed to Table 18, it is 71.2eV Pt. 4f<sub>7/2</sub> binding energy were conventionally measured with the catalyst (sample P3A). Pt The measured value of 4f binding energy, Peak hwhm (half width at the time of the one half of a peak price), and peak intensity are Pt of Pt(0) oxidization condition (namely, Pt metal). The theoretical value of 4f peak and the value of a XPS model handbook were approached, and it was in agreement. These values are Pt of the catalyst by this invention. It was used in order to make 4f peak in agreement with a curve (curve fitting).

[Table 18]

表 18. Pt/C パウダーの XPS データ

実施例	Pt 4f <sub>7/2</sub> ピーク位置 (eV)	I (Pt4f) / (C 1s) (相対強度)	I (N 1s) / (C 1s) (相対強度)
P3A*	71.2	0.682	0.028 (1.5 at.%)
P27B	71.2 (80%) 72.5 (20%)	0.305	0.000
P31C	71.4	0.481	0.020 (1.0 at.%)
P32A	72.1 (80%) 73.2 (20%)	0.398	0.000
P32B	73.4	0.352	0.149 (5.6 at.%)
P33B	73.3	0.406	0.165 (7.0 at.%)
P37C	71.8	0.489	0.009 (0.4 at.%)
P38A	71.6	0.525	0.000
P39A	71.7	0.327	0.000
P39B	71.6	0.234	0.022 (1.1 at.%)
P40C	71.9	0.327	0.025 (1.3 at.%)

\* 従来技術

Including the information about I(Pt 4f)/I (C 1s) specific strength, Table 18 can use this again in order to measure distribution of Pt cluster on carbon support. Since all almost contain Pt of the same amount as example P3A (20 % of the weight), specific strength I (Pt 4f)/I (C 1s) can be used in order [ of an example ] to compare distribution of Pt directly as contrasted with it of a commercial catalyst. This is the most exact for the catalyst of this invention which has the surface area which is equal to the thing prepared by the spraying conversion temperature of 300 degrees C in a commercial catalyst, for example, nitrogen, and more than it, and the thing

prepared by 400 degrees C and more than it in air.

[0376]

Moreover, the specific strength  $I(N\ 1s)/I(C\ 1s)$  of all the catalysts analyzed by XPS to Table 18 and the surface concentration of the nitrogen in atomic % are enumerated. In example P3A (conventional technique), this suggests existence of a nitrogen content surfactant to preparation of a catalyst including a small amount of nitrogen impurity, having used nitrogen content drugs.

[0377]

Pt of example P27B It is Pt only by using the double line (doublet) about Pt (0) oxidation state so that 4f spectrum may see. 4f peak was not able to be made in agreement with a curve. Pt It is Pt in 72.5eV of binding energy of 4f7/2 peak. The 2nd double line of 4f peak is required. This Pt 4f7 / 2 binding energy should relate to Pt (II) oxidation state, and have suggested that conversion to the metal Pt of Pt precursor is not perfect in example P27B. The specific strength of the 2nd double line of Pt (II) oxidation state is Pt. About 20% of the whole 4f peak area was occupied, therefore 20% of Pt in example P27B was not changed into Pt (0) oxidation state, and spraying conversion at 400 degrees C in air did not return Pt precursor to Pt (0) completely, but it has suggested not distributing Pt good on carbon support. The value of the specific strength  $I(Pt\ 4f)/I(C\ 1s)$  of example P27B is low more than twice compared with it of a commercial catalyst. However, the nitrogen impurity was not detected by example P27B.

[0378]

Please care about that it is required for the fuel cell catalyst of Pt base in order that Pt metal cluster which it was supported on carbon and distributed to altitude may attain the high activity of a catalyst. Therefore, it can make to attain advanced Pt distribution of Pt (0) condition into criteria when predicting the catalyst engine performance of a fuel cell catalyst.

[0379]

In order to find out the optimal spraying conversion conditions of attaining perfect Pt reduction and high distribution, change of these properties was analyzed as correlation of spraying conversion temperature and a carrier gas presentation. Generally, it is Pt. Shifting to the one where the location of 4f7/2 peak is higher than 71.2eV of binding energy has suggested the imperfection of reduction of Pt metal. To coincidence, distribution of Pt cluster has suggested the low thing, and  $I(Pt\ 4f)/I(C\ 1s)$  specific strength lower than a commercial catalyst is in agreement also with the mean particle diameter of Pt cluster being large at it. In example P38A, in order to evaluate a measurement accuracy, XPS analysis was repeated. The comparison of two analysis showed the repeatability which was excellent in the XPS peak location, and the difference in XPS specific strength was less than 2%.

[0380]

Drawing 65 is Catalyst (it generated from  $Pt(NH_3)_4(NO_3)_2$  precursor) Pt. The dependency as correlation of the spraying conversion temperature and a carrier gas presentation of 4f7 / 2 binding-energy location is expressed. In order [ to Pt (0) oxidation state ] to attain high conversion moderately, the conversion temperature of about 500 degrees C is required at least, using air as carrier gas. A big difference is not seen when using nitrogen as carrier gas. Even if it raises conversion temperature to 700 degrees C, a result does not improve. It seems that therefore, the temperature of about 500 degrees C is enough to change a precursor completely and generate a metal Pt kind when using  $Pt(NH_3)_4(NO_3)_2$  precursor for a formula.

[0381]

The high resolution XPS spectrum which measured example P32B and example P33B supports the conclusion. Although both of the catalysts were manufactured at the conversion temperature of 200 degrees C, in example P32B, air was used as carrier gas and example P33B used nitrogen as carrier gas. It adds to Pt (II) oxidation state, for example, the peak in 73.2eV of the precursor changed partially, and they are other Pt(s). 4f peak double line is Pt. It appears by 4f7 / about 75.6eV of 2 binding energy, and this is very close to the value of Pt (IV) oxidation state. N In 1s field, a peak is observed by 404.2eV and 406.5eV, and the conclusion that conversion of a precursor is imperfect is checked about NO2 and three sorts of NO(s). By this imperfect conversion, the nitrogen concentration in these catalysts also becomes 7 atom %.

[0382]

conversion temperature -- 300 degrees C -- raising (example P32A) -- nitrogen impurities decrease in number greatly. However, although conversion of a precursor is more perfect, Pt of Pt (II) oxidation state is about 20%.

[0383]

As mentioned above, distribution of Pt cluster is very important in order to attain whenever [ high catalytic activity ]. Drawing 66 expresses the dependency of specific strength I (Pt 4f)/I (C 1s) as a function of spraying working temperature. Generally, with the same spraying working temperature, the catalyst made as carrier gas using nitrogen shows the high specific strength I (Pt 4f)/I (C 1s), therefore obtains good distribution of Pt by the carrier surface top. If spraying working temperature is raised to 500 degrees C, improvement in Pt distribution will be brought about with both air and nitrogen as carrier gas. The rise to 700 degrees C of spraying working temperature does not become useful to Pt distribution. In example P38A prepared with the working temperature of 500 degrees C in nitrogen, the value of the highest specific strength I (Pt 4f)/I (C 1s) is observed. It suggests that the specific strength I (Pt 4f)/I (C 1s) 0.525 of example P38A is lower than the value which measured sample P3A, and distribution is low. However, the nitrogen impurity was not detected by example P38A, but, on the other hand, the impurity of about 1.5 atoms % was detected by sample P3A.

[0384]

Two of the samples mentioned to Table 18 compounded Pt with a different Pt precursor ( $\text{H}_2\text{Pt}_6(\text{OH})$ ) included only 10% of the weight. The XPS data of example P39B and P40C express that it is required in order that the reaction temperature of at least 400 degrees C may acquire Pt (0) oxidation state from this precursor in air. Pt of example P40C prepared at 300 degrees C has distribution higher than example P39B prepared at 400 degrees C. The high conversion temperature of this result is contrastive with the XPS data of the sample which brings about better Pt distribution and which used  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  precursor as the base.  $\text{H}_2\text{Pt}(\text{OH})_6$  precursor changes this result at lower temperature compared with  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ , and it suggests that the diffusion and the condensation of Pt cluster which are not desirable occur at hotter conversion temperature.

[0385]

XPS analysis of electrode catalyst powder offers the information about the property of important catalysts, such as an oxidation state of Pt, distribution, etc. which affect the catalytic activity of a powder object. However, other properties, such as distribution of Pt cluster size, will have remarkable effect on the activity of a catalyst similarly.

[0386]

TEM data show the remarkably good thing compared with example P31C in which the distribution of the cluster size of the whole example P38A which carried out spraying conversion at 500 degrees C in nitrogen carried out spraying conversion at 500 degrees C in air. In accordance with the XPS data of Pt distribution, especially as for this observation, it is checked that carrier gas affects generation and Pt distribution of a catalyst.

[0387]

It compared with two electrode catalysts which evaluate the sample of a Pt/C electrode catalyst by the PEM fuel cell, and can obtain the electrochemical characterization in a commercial scene. Characterization beam examples are example P37C, P38A, P39A, and P39B electrochemically.

[0388]

The gas diffusion electrode was manufactured by the catalyst ink method. The Pt/C catalyst was distributed in the solution of NAFION (trademark) / alcohol / water, and stable ink suspension was obtained. The 1g electrode catalyst was mixed to 2ml i-propanol (in order to avoid the exoergic effectiveness, after soaking in little water), and the bought-in 10ml NAFION (trademark) solution (water / 5 % of the weight of polymers in i-propanol mixture) was made to specifically suspend. This ink is maintained during electrode preparation, in order to bring about the catalyst / NAFION (trademark) ratio of 2:1 and to incorporate an electrode catalyst particle to the electrolyte membrane of a NAFION (trademark) polymer.

[0389]

A gas diffusion electrode is SHAWINIGAN. It is prepared by brush coating so that it may become 35 - 40% of the weight of TEFRON / carbon ratio on a carbon cloth about the suspension of MLACK and a TEFRON emulsion (E. I. du Pont de Nemours (DuPont)). The gas diffusion electrode soaked in TEFRON (trademark) / carbon suspension is heat-treated at 300 degrees C - 350 degrees C for 1 hour. This temperature requirement is close to the glass transition point of a TEFRON (trademark) ingredient.

[0390]

When an electrode is carried on a 90-100-degree C hot platen, coating of Pt / the carbon-electrode catalyst ink is

carried out with a brush on an impregnated fabric. Subsequently, an electrode is processed at 155 degrees C near the melting point of a NAFION (trademark) ingredient in air for 20 to 30 minutes. Support of a catalyst is determined from the weight of an electrode.

[0391]

Although the amount of platinum support of an anode plate (Pt loading) was  $0.20 \pm 0.01$  mg/cm<sup>2</sup>, it is thought that this is low as an industrial standard of an oxygen electrode catalyst. 10% of Pt/C marketing catalyst was used for all hydrogen electrodes (anode plate), and 0.05mg /of platinum of 2 was supported cm.

[0392]

A membrane electrode assembly (MEAs) is NAFION (trademark) symmetrically (a catalyst side faces the film) about an electrode. The heat press was carried out at 200 degrees C at the both sides of PEM of 112 (C G processing company (CG Processing, Inc.)), from the catalyst bed, melting of the film and the NAFION (trademark) ingredient was carried out, and they were manufactured. The reactant gas of the atmospheric pressure which gave area 2 or 50 degrees C and moisture of 50cm of operation between the side plates of a graphite plate with a rib and copper in the trial cel performed the performance evaluation of MEAs.

[0393]

Drawing 67 shows the comparison of the voltamogram (votamograms) (plot of cell potential pair current density) of MEAs which prepared and measured the catalyst by a different commercial catalyst (sample P4A and P5A) and different this invention on the same conditions. The result was obtained on the same carbon black support with the electrode catalyst containing 20% of the weight of platinum. It is clear from these curves to express the engine performance in which the electrode catalyst of this invention was excellent in MEA. The numerical expression of this excellency is drawn from the current density corresponding to cell potential 0.6V. Although, as for the conventional electrode catalyst, both give 400 mA/cm<sup>2</sup>, the electrode catalyst of this invention gives 600 mA/cm<sup>2</sup>, and its engine performance of MEA of cell potential 0.6V is improving 50%.

[0394]

It means that drawing 67 shows overall more high current density over the whole range of the potential which the electrode produced with the electrode catalyst of this invention investigated. A thing with the low (there are few curved negative inclinations in a "straight-line" part) dependency of a current [ as opposed to potential in a polarization curve ] is the description, and this shows that ohmic resistance of a catalyst bed is low to coincidence. The dependency of the potential to current density shows that the limitation of diffusion does not appear in the range of the current density which maintained and investigated parenchyma top linearity also in high current density.

[0395]

Drawing 68 is the TAFERU Fig. of the data from the low current field of drawing 67 . a TAFERU Fig. establishes the device of a reaction (from the negative inclination of the straight-line-ized dependency), and it uses it in order to clarify effectiveness of the catalyst expressed in the location of the intercept on a current density shaft -- a half -- it is the data representation of - logarithm. In order to save an amount, convenience can improve the emission gas from a reactor, or its part reuse. The gas which carries out reuse can be processed in order to remove a component without the need, and fresh H<sub>2</sub>. It is shown that drawing 68 is what is depended on catalytic activity with the advantageous high engine performance of the catalyst which generally became clear in drawing 67 . All of these three curves are the straight lines which have the same negative inclination (on a half-logarithm coordinate), and they suggest the uniform device of oxygen reduction. However, the curve corresponding to the electrode catalyst of this invention is shifted to the direction of high current density with the forward intercept difference of current density \*\*\*\*\* 30 mA/cm<sup>2</sup>. As for the sample of the conventional technique, both show the same catalytic activity on parenchyma.

[0396]

The distribution on the path of a platinum cluster and its carbon support can explain the catalyst engine performance whose electrode catalyst of this invention improved compared with the sample of the conventional technique. The SEM enlargement of the electrode catalyst of this invention in comparison with the electrode catalyst of the conventional technique shows that the electrode catalyst of this invention has the platinum cluster (1-2 micrometers) of very a lot of diameters of minute compared with the sample of the conventional technique. This brings about use of the platinum in the inside of the barrier layer of an oxygen electrode, and the increment in a reaction interface.

[0397]

Drawing 69 compares with the research sample which has the best engine performance in which this invention person gets to know the polarization curve obtained with the Pt/C catalyst (20 % of the weight of Pt(s)) of this invention, and a Pt-Co-Cr/C complex electrode catalyst (sample P6A). Coating is carried out to an electrode surface so that this catalyst may be measured with the metal Pt per cm<sup>2</sup> and it may become the same amount of support. As few [ 3 times ] catalysts as A [ sample P6 ] are supported to an electrode for the amount of Pt(s) in the electrode catalyst of this invention. It means that both polarization curves are in agreement on parenchyma, and its simpler Pt electrode catalyst of the engine performance of 3 metal complex catalyst and this invention which progressed corresponds wonderfully.

[0398]

Drawing 70 compares the polarization curve obtained with the electrode catalyst (sample P7A) of other conventional techniques with the example of this invention which has the same Pt content. A curve is obtained for 0.21 mg/cm<sup>2</sup> and the electrode catalyst of this invention at sample P7A by Pt support from which 0.11 mg/cm<sup>2</sup> differs. Coincidence of a curve is observed when Pt support of the electrode catalyst of this invention is the amount of the abbreviation one half of a commercial catalyst. This suggests the commercial big advantage of this invention clearly. The amount of Pt used decreases remarkably, without Pt / carbon catalyst being able to attain the same engine performance with the catalyst ingredient of a half amount, therefore spoiling the engine performance.

[0399]

Drawing 71 shows the engine performance when using atmospheric air for supply to the oxygen gas diffusion electrode in a cel about two examples of this invention of having a different Pt content. The electrode catalyst with low (10%Pt / carbon) Pt content gives low current density compared with what has a high (20%Pt / carbon) metal content so that it may be expected. However, it should care about having obtained this curve with the electrode which made the total amount of Pt the same and prepared it. That is, coating of the sample with low Pt content is carried out using the twice as many amount of catalysts as this. However, the engine performance of an electrode catalyst in which it fell is in the level still obtained with the electrode catalyst of the conventional technique (compare drawing 71 with drawing 67 ). The sample curve of 10%Pt / carbon of this invention laps with the sample curve of the conventional technique of 20%Pt / carbon.

[0400]

Drawing 72 has been obtained by the same MEA as drawing 71 , and the engine performance when using oxygen for supply to the oxygen gas diffusion electrode in a cel is shown about the electrode catalyst of this invention which has a different Pt content. Especially the thing for which pure oxygen is passed through an electrode eliminates a limit of mass migration greatly in that in which a macro-diffusion process (macro-diffusion process) is involved. Although the curve obtained with an electrode catalyst with low Pt content (10% Pt / carbon) is obtained from a catalyst with a high (20%Pt / carbon) metal content, it is shifted to near. Therefore, drawing 72 means that the thickness of the catalyst bed formed in the low engine performance (it is shown in drawing 71 like) of a sample 10% using the ingredient of the amount of 2 double is involving. This is checked by the TAFERU Fig. of the data (here, the catalyst engine performance is not covered by the migration process) in a low current consistency as shown in drawing 73 .

[0401]

The purpose of the example of the following additions is clarifying the optimal structural parameter of a lot which gives the electrode catalyst which has activity most for the oxygen reduction reaction in the air cathode of a proton exchange film oxygen reduction fuel cell (PEMFC). Depending on the oxidation state of platinum, and distribution, as for the activity of an electrode catalyst, this is influenced according to the class of the conditions of a spraying translation process, carrier gas, a precursor salt, and carbon support.

[0402]

Evaluation of a Pt/C electrode catalyst was finished with electrochemical evaluation by various techniques, such as nitrogen adsorption (BET), XRD, TEM and XPS, and CO chemisorption.

[0403]

Many examples were prepared as follows. 104AO(s)2 are SHAWINIGAN. It is the sample which consists of 10% of the weight of Pt on BLACK (trademark), and has 6.3nm Pt microcrystal and amount of Pt support 1.43 mgPt/cm<sup>2</sup>. 156AO(s)2 are SHAWINIGAN. It is the sample which consists of 20% of the weight of Pt on



BLACK (trademark), and has 5.2nm Pt microcrystal and amount of Pt support 2.66 mgPt/cm<sup>2</sup>. 158BO(s)<sub>2</sub> are samples which consist of 10% of the weight of Pt on VULCAN(trademark) XC-72, and have 4.6nm Pt microcrystal and amount of Pt support 1.23 mgPt/cm<sup>2</sup>. 142AO(s)<sub>2</sub> are samples which consist of 20% of the weight of Pt on VULCAN(trademark) XC-72, and have 11.4nm Pt microcrystal and amount of Pt support 2.95 mgPt/cm<sup>2</sup>.

[0404]

The example was examined in the alkali electrolyte and the TAFERU Fig. was obtained. SHAWINIGAN It turns out that BLACK (trademark) is the engine performance better than VULCAN(trademark) XC-72. Smaller microcrystal size is the engine performance better than big microcrystal size (it asked by the X diffraction).

[0405]

Moreover, the purity of the dispersed phase on a carbon front face is important when opting for the engine performance of a powdered electrode catalyst. The usual solution precipitate process used in order to manufacture the carbon support electrode catalyst of the noble-metals base uses the chemical or surfactant containing sulfur. It is poison and, as for sulfur, the residual sulfur of few amounts of traces also invites the remarkable fall of the engine performance to the catalytic activity of Pt. The ligand, complex chemical, or surfactant containing the component which checks the activity of the last catalyst does not need to be used for the ingredient manufactured according to the process of a publication on these specifications. As a result, a process given in this specification brings about the ingredient of the purity of a high level.

[0406]

It analyzed in order to compare the platinum of 10 % of the weight on carbon, and 20% of the weight of a commercial catalyst with the catalyst of this invention. It prepared by one of the paths of four sorts of fuel cell catalysts of this invention. They are an ultrasonic transducer (a single and plurality), a spray drier, an ultrasonic spraying nozzle, and post processing at chronologic order.

[0407]

All the samples were similarly prepared irrespective of the processing system to be used. It diluted with water, kneading a carbon distribution object first (shear mix), and the metal salt which subsequently dissolved was added slowly. The precursor distribution object was kneaded for 10 minutes, the additional salt was added, and homogeneous distribution was secured.

[0408]

The sample enumerated to Table 19 was prepared through the ultrasonic transducer, the sample enumerated to Table 20 used the ultrasonic spraying nozzle, and the sample enumerated to Table 21 was manufactured with the spray drier.

[Table 19]

表 19. 超音波トランスデューサを用いて生成したサンプル

サンプル	組成 (wt. %)	カーボン 支持体	Pt 前駆体	炉の温度 (℃)	表面積 (m <sup>2</sup> /g)
PPC087071A	20% PT	グラホ 1300	Pt(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	90
PPC097001A	20% PT	グラホ 1300	H <sub>2</sub> Pt(OH) <sub>6</sub>	450	80
PPC056071A	20% PT	グラホ 1300	H <sub>2</sub> Pt(OH) <sub>6</sub>	350	62
PPC056071B	20% PT	グラホ 1300	H <sub>2</sub> Pt(OH) <sub>6</sub>	250	42
PPC056072A	20% PT	グラホ 1300	H <sub>2</sub> Pt(OH) <sub>6</sub>	300	44.9
PPC056072B	20% PT	グラホ 1300	H <sub>2</sub> Pt(OH) <sub>6</sub>	400	66
PPC097120A	50% PT	グラホ 1300	Pt(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	--
PPC097120B	60% PT	グラホ 1300	Pt(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	12.9
PPC093088A	20% PT	グラホ 1300	Pt(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	--
PPC093088B	20% PT	グラホ 1300	Pt(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	550	--
PPC093089A	20% PT	グラホ 1300	Pt(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	600	--
PPC093090A	20% PT	グラホ 1300	Pt(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	650	--

[Table 20]

表 20. 超音波スプレーノズルによって生成された電極触媒

サンプル	組成 (wt. %)	カーボン 支持体	Pt 前駆体	炉の温度 (°C)	表面積 (m <sup>2</sup> /g)
PPC093101A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	550	52
PPC093101B	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	600	---
PPC093101C	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	625	---
PPC093102A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	650	60
PPC093102B	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	700	---
PPC093102C	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	675	---
PPC093101A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	550	---
PPC093101B	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	600	---
PPC093101C	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	625	---
PPC093104A	20%Pt, 10%懸濁	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	550	---
PPC093104B	20% Pt 10%懸濁	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	600	---
PPC093104C	20% Pt 10%懸濁	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	650	---
PPC093104D	20% Pt 10%懸濁	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	700	---
PPC093109A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	---
PPC093109B	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	600	---
PPC056087A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	48
PPC056091A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	425	52
PPC056092A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	450	52
PPC056093A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	475	49
PPC056094A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	400/500/400	---
PPC056095A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	400/450/500	---
PPC056096A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	50
PPC056097A	60% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	31
PPC056099A	10% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	---
PPC056100A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	---
PPC056101A	40% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	38
PPC056102A	60% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	30
PPC056103A	5% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	56
PPC056104A	10% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	52
PPC056105A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	49
PPC056106A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	500	44
PPC056111A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	400	45
PPC056112A	20% Pt	グラホ 1300	Pt (NH <sub>3</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub>	425	44

PPC056113A	20% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	450	48
PPC056114A	20% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	475	47
PPC056115A	20% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	350	--
PPC056126A	20% Pt	グラホ 1322	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	500	--
PPC056140A	20% Pt	グラホ 1300	$\text{H}_2\text{PtCl}_6$	500	--
PPC056141A	20% Pt	グラホ 1300	$\text{H}_2\text{PtCl}_6$	500	47
PPC056142A	20% Pt	グラホ 1300	$\text{H}_2\text{PtCl}_6$	350	47
PPC056143A	20% Pt	グラホ 1322	$\text{H}_2\text{PtCl}_6$	500	35
PPC056146A	20% Pt	グラホ 1322	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	300	--
PPC056153A	20% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	500	52
PPC056154A	20% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	500	48
PPC056155A	20% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	500	52
PPC056156A	20% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	500	53

[Table 21]

表 21. 噴霧乾燥機で生成された触媒

サンプル	組成 (wt. %)	カーボン支 持体	Pt 前駆体	入口／出 口温度 (°C)	表面積 (m <sup>2</sup> /g)
PPC097108C	20% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	600F	--
PPC056138A	20% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	646F	--
PPC056138B	20% Pt	グラホ 1322	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	639F	32
PPC056138C	20% Pt	グラホ 1322	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	552F	26
PPC056139A	20% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	538F	18
PPC056157A	20% Pt	グラホ 1322	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	482/244	70
PPC056157B	20% Pt	グラホ 1322	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	427/227	--
PPC056157C	20% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	482/249	38
PPC056157D	20% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	427/227	--
PPC056158A	5% Pt	グラホ 1322	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	518/274	125
PPC056158B	10% Pt	グラホ 1322	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	517/265	108
PPC056158C	40% Pt	グラホ 1322	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	521/279	64
PPC056159A	5% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	513/274	66
PPC056159B	10% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	515/274	53
PPC056159C	40% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	514/282	40
PPC056163C	20% Pt	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	526/282	46
PPC056164A	20% Pt 10% susup	グラホ 1300	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	524/287	48
PPC056164C	20% Pt	グラホ 1322	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	524/287	104
PPC056165A	20% Pt 10% 固体	グラホ 1322	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	524/282	104
PPC056166C	20% Pt	グラホ 1322	$\text{H}_2\text{PtCl}_6$	523/284	--
PPC056167A	20% Pt	グラホ 1300	$\text{H}_2\text{PtCl}_6$	523/283	--

Drawing 74 expresses the reverse relation between platinum support and surface area. Since per gram of a catalyst normalizes surface area and support of Pt increases (the consistency of Pt is high compared with it of carbon support), this result is expected. However, if the same carbon support (SHAWINIGAN BLACK (trademark)) is used, it is important for change of the surface area of the catalyst generated with an ultrasonic

spraying nozzle and a spray drier to care about the almost same thing. VULCAN (trademark) In support with larger surface area than those, such as XC-72, this effectiveness shows up more strongly for the low consistency of carbon support.

[0409]

Although spraying conversion temperature must be high enough in order to change platinum, there is nothing then so highly that carbon burns. It is shown that powdered surface area increases drawing 75 as temperature rises. Although it suggests that this uses the highest possible temperature, loss by combustion of the carbon in an elevated temperature must also be taken into consideration.

[0410]

Generally it is admitted that the increment in the metal Pt cluster on carbon support brings about the increment in catalytic activity. Extent of surface metal distribution is influenced with the surface area of the metal salt to be used, metal support (metaled weight %), and carbon support. If the amount of metals on a carbon front face is made to increase, big metal microcrystal is brought about, therefore distribution becomes low, and, naturally the front face of the metal to expose becomes small. The carbon to be used also influences process temperature. It is believed that high surface area becomes low decomposition temperature. SHAWINIGAN BLACK (trademark) opposite VULCAN (trademark) Processing of XC-72 is compared and one example is shown. It is SHAWINIGAN about 20% of the weight of platinum. BLACK (trademark) and VULCAN (trademark) When it is processed at 210 degrees C on XC-72, the increment in conversion is SHAWINIGAN of low surface area. VULCAN of high surface area [ BLACK / (trademark) ] (trademark) It saw on XC-72. This has suggested that conversion temperature can be made still lower by using the carbon of more high surface area like about 800m<sup>2</sup>/g. Probably, it will also be useful to use the mixture of the carbon support which has different surface area. If the carbon support of high surface area changes at low temperature, since it will work as a catalyst to conversion of the carbon of low surface area, this has an advantage as a catalyst.

[0411]

It was used as quick preliminary screening which supervises that a precursor salt changes a powder X diffraction (XRD) spectroscopy into the activity catalyst condition. The manufacture process was optimized as instant feedback of process condition fine tuning using XRD. XRD does not require an effort rather than an electrochemical trial or electrochemical TEM. Therefore, when it was decided that powder will have the possibility as a catalyst once, they were applied to the electrochemical trial. This enabled quick optimization of processing conditions.

[0412]

That existence of a platinum peak was shown in sample PPC056156A by XDR suggests that the platinum precursor was changed into metal platinum.

GURAHO dried at the room temperature 1300, platinum precursor Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>, and GURAHO The XRD pattern of the mixture of 1300 and Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> also came to hand. This series shows that the diffraction pattern of a start ingredient (GURAHO 1300 and Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>) is not addition-like only, if it mixes. The interaction of two compounds makes the dry precursor distribution object produce a completely new diffraction pattern. The diffraction pattern looked at by the precursor distribution object dried at the room temperature is the same as that of it of the catalyst powder processed into the forge fire which changes an elevated temperature, however a platinum precursor at the temperature which is not high. The platinum in sample PPC056093A does not have the peak of the property of platinum, and is not changed into metal platinum.

[0413]

The X diffraction pattern used the mean particle diameter (S) of the platinum microcrystal in a powder sample for evaluating by the formula of Scherrer (Sherrer) and Warren (Warren), respectively.

[Equation 3]

$$S = \frac{0.9\lambda}{B \cos \theta_{\max}}$$

$$B^2 = B_M^2 - B_S^2$$

lambda is [ the breadth of a radian of the spectral line and thetamax of X-ray wavelength (it is 1.54056A at Cu)

and B ] the Bragg angles (Bragg angle) among a formula. Radian [ in / in BM / half height (FWHM) ] measurement peak width and BS are FWHM corresponding to the peak of KCl used as a criterion. By all measurement, FWHM of Pt <111> peak in about 39-degree 2-theta (theta) was used.

[0414]

The magnitude of microcrystal is inversely proportional to distribution of the platinum on carbon support. The metal generally high-distributed brings about high catalytic activity. Therefore, the magnitude of platinum microcrystal was used to evaluate distribution of the platinum on carbon support. Cautions are required to interpret these results. It is the catalyst which has being [ it / big microcrystal ] \*\*\*\* and a sharp XRD peak, and the inspection by TEM also showed clearly that there is microcrystal which many are fine and was distributed further. The signal of bigger microcrystal carried out the mask of the weak large signal from the microcrystal which existed too and which is distributed finely.

[0415]

Drawing 76 shows the microcrystal size of platinum, and the relation between Pt<111> FWHW(s). This theoretical plot was drawn from the formula of Scherrer (Sherrer) and Warren (Warren) using the values 0.3-2.5 of FWHW. Microcrystal size was inversely proportional to FWHW so that it might be shown.

[0416]

Drawing 77 is SHAWINIGAN of peak breadth. The dependency to the platinum support on BLACK (trademark) is shown. A plot expresses the breadth [ % of the weight / of Pt(s) / 10 - 20 ] of the time max, and shows the optimal microcrystal size.

[0417]

It was shown that the platinum content is increasing the first elemental analysis from what manufactured medicine. This processed the catalyst in nitrogen and was made to go to examination which makes small possibility of the carbon combustion with such high working temperature. By installing the gas line from a liquid nitrogen tank instead of air Rhine, application of the system which uses nitrogen carrier gas was finished. It became possible to prevent contacting interspace mind that use nitrogen gas for both a carrier and coolant gas, and it is put to the elevated temperature by this in the catalyst.

[0418]

It was proved that the result that air excelled in the structure target was induced through these experiments. Emphasizing this point, therefore using nitrogen as carrier gas abandoned electrochemical data. Seemingly, the engine performance which was excellent in the catalyst generated in air will be based on existence of the oxygen which helps disassembly of the ligand of a platinum precursor, a carbon distribution binder, and a surfactant. It seems that the catalyst front face was polluted with these organic substance that cannot be disassembled when nitrogen was used. Combustion of carbon is microscopic and it turned out that this misunderstanding was produced with the concentration of the carbon distribution object reported accidentally later.

[0419]

To drawing 78, the X diffraction peak of Pt<111> FWHM to whenever [ coke-oven-temperature / of the catalyst made from both in air and nitrogen ] was plotted. The parameter of FWHM was used for distributed evaluation of Pt microcrystal, and distribution of Pt kind on a carbon carrier surface was so high that FWHM was high. At the temperature of a 500 degrees C - 600 degrees C field, when air was used as a carrier and coolant gas, the value of FWHM became larger than that of nitrogen, therefore better Pt distribution was obtained as a carrier and coolant gas using air.

[0420]

The related Fig. of the amount of a precursor and a carrier surface product is shown in drawing 79. This model compared the area of Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> with the surface area of predetermined carbon support. It calculated to the carbon support which is three which surface area increases based on weight % of platinum. The surface area of the used carbon support is 80,240,800m<sup>2</sup>/g, and 2.25nm of area of Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> molecule was estimated at 2. If the gross area covered by Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> is the same as it of carbon, the carbon front-face top should become the precursor molecule of a monolayer (monolayer). This will not serve as a monolayer of platinum, since the ligand of Pt precursor occupies the great portion of precursor area. Therefore, the small cluster of each Pt atom which kept spacing enough, or a platinum atom will surely be formed. Additional Pt (NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>) dyad becomes two or more layers, and the dyad possibility of bigger coagulum formation than

that metaled increases. It will become a catalyst with activity lower than it which has small metal microcrystal, since all on the front faces of carbon will be covered and metaled surface area will decrease, if this idea is followed, and there is enough much metaled support.

[0421]

The insertion Fig. of drawing 79 is 20% of the weight of platinum, and when the surface area of carbon decreases to 800 to 240 or 80m<sup>2</sup>/g, it is shown that a number of layers increases to 2.12 and 6.36 from 0.64. This suggests that no platinum support is the optimal to predetermined carbon surface area. Furthermore, each carbon has the ideal field (window) of metal support, and it makes it possible to make a Pt/C catalyst according to the demand of support. This point becomes clearer as metaled support increases. In order to avoid this possibility, it should connect to an experimental result, and although it is impossible to predict whether it becomes so large that metal support covers all the particles with which point, carbon should be chosen so that the number of layers may become min.

[0422]

From the temperature limitation of the conventional spray drier, the substitute path of changing a platinum precursor is needed. After drying powder below with working temperature required for reduction of platinum, it applied to down stream processing of addition of powder. the inside of the furnace of various ambient atmosphere presentations which carried out preheating of the sample -- five -- or it put in for 10 minutes. The ambient atmosphere of a furnace was either of the 2 latters of air, hydrogen, nitrogen, or some ratios. The result of post processing is collectively shown in Table 22.

[0423]

The first experiment in air shows the thing with the important balance between temperature and time amount which a small field exists. If a catalyst is put to too much high temperature or too much low temperature long time, platinum will be coagulated in remarkable magnitude. This coagulum is exaggerated by existence of hydrogen. The comparison of sample PPC113121A and PPC11386B shows the reducing power of hydrogen. Although afterbaking of the sample PPC113086B was carried out at 250 degrees C and not being changed in air, platinum not only changed, but the magnitude of microcrystal was observed by max when the same powder was processed in hydrogen at 150 degrees C like PPC113121A. This originated in the platinum kind which is easy to move by the elevated temperature existing partially under existence of hydrogen. It was made difficult that this migratory kind narrowed after-treatment conditions. After treatment was abandoned once what the spray drier will solve the transformation problem of platinum for with the reducing agent could understand, when this kind was discovered by reference.

[0424]

For calculation of Pt microcrystal size listed to Table 22, count of microcrystal size is [ XRD being data and ] more specifically due to the comparison with a criterion based on FWHM of the XRD peak of Pt <111>.

[Table 22]



表 2 2. 後処理の処理条件

サンプル	温度	転化	結晶子サイズ (Å)	雰囲気
PPC113086A	300	有	134.070	空気
PPC113086B	250	無	--	空気
PPC113086C	275	有	136.030	空気
PPC113087A	250	有	79.230	空気
PPC113087B	275	有	87.240	空気
PPC113087C	300	--	--	空気
PPC113088A	250	無	--	空気
PPC113088B	275	有	77.130	空気
PPC113088C	300	有	113.370	空気
PPC113089A	300	有	165.620	空気
PPC113090A	250	無	--	空気
PPC113090B	250	有	71.210	空気
PPC113090C	250	有	85.520	空気
PPC113092A	250	無	--	空気
PPC113092B	275	有	121.880	空気
PPC113092C	300	有	124.450	空気
PPC113093A	250	無	--	フォーミングガス
PPC113093B	250	一部	--	フォーミングガス
PPC113093C	250	有	181.220	フォーミングガス
PPC113094A	200	無	--	フォーミングガス
PPC113094B	225	一部	--	フォーミングガス
PPC113100A	250	燃焼	--	空気
PPC113100B	250	無	--	空気
PPC113100C	275	一部	--	空気
PPC113114A	250	有	282.31	H <sub>2</sub>
PPC113117A	100	無	--	空気
PPC113117B	200	有	197.84	H <sub>2</sub> /N <sub>2</sub>
PPC113121A	150	有	212.72	H <sub>2</sub> /N <sub>2</sub>
PPC113121B	25	無	--	H <sub>2</sub> /N <sub>2</sub>
PPC113133A	150	無	45.45	空気
PPC113133B	200	有	83.07	空気
PPC113135A	200	大部分	74.12	空気
PPC113135B	250	無	48.93	空気
PPC113135C	250	有	83.46	空気
PPC113135D	275	一部	60.71	空気

By the preparation approach of the conventional technique of a platinum catalyst, since it is cheap, a platinum chloride precursor is used. Most platinum catalysts manufactured according to this invention used Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (platinum amine), in order to avoid the corrosion of the system which may happen common to use of a chlorine ion. A chloride is acidity and makes the binder of a carbon dispersing element solidify with a solution again. It becomes an unstable dispersing element by coagulation of a binder, and hardens within 1 hour. In this reason, an amine is the salt of the precursor most often used.

[0425]

However, conversion temperature falls by using the precursor of a chloride from about 400 degrees C to less than 350 degrees C. This became a key point when the interest was leaned, in order that a spray drier might try manufacture of a platinum catalyst.

[0426]

Use of a reducing agent serves as instead of [ of after treatment ]. When it cannot raise with the conventional spray drier to temperature required for reduction of platinum, an additive can be used so that reduction may take place at low temperature more. By this approach, desiccation/calcining is still one process, and solves some problems accompanying after treatment. The experiment conditions and reducing agents which were used for manufacturing a platinum-electrode catalyst to Table 23 are enumerated.

[Table 23]

表 23. 還元剤を探す実験条件

サンプル	組成 (wt. %)	カーボン支持体	前駆体	温度 (°C)	転化
PPC097109B	20%Pt, 1 eq HCOOH	グラホ 1300	アミン	600F	無
PPC097109A	20%Pt, 1 eq HCOOH	グラホ 1300	アミン	400F	無
PPC097110A	20%Pt, 4 eq HCOOH	グラホ 1300	アミン	600F	無
PPC097109C	20%Pt, 4 eq HCOOH	グラホ 1300	アミン	400F	無
PPC113013B	20%Pt, KBH <sub>4</sub>	グラホ 1300	塩化物	600F	--
PPC113013C	20%Pt, 尿素	グラホ 1300	塩化物	400F	--
PPC056098A	20%Pt, KBH <sub>4</sub>	グラホ 1300	アミン	200	--
PPC056116A	20%Pt, 10%EtOH	グラホ 1300	アミン	350	大部分
PPC056117A	20%Pt, 過剰 NaOOC	グラホ 1300	アミン	350	大部分
PPC056118A	20%Pt, 10%EtOH	グラホ 1300	アミン	400	小ビーク
PPC056119A	20%Pt, 10%MeOH	グラホ 1300	アミン	350	大部分
PPC056120A	20%Pt, 10%HCOOH	グラホ 1300	アミン	350	大部分
PPC056121A	20%Pt, 10%MeOH	グラホ 1300	アミン	300	一部
PPC056122A	20%Pt, 10%MeOH, 10%HCOOH	グラホ 1300	アミン	300	一部
PPC056141A	20%Pt, 10%EtOH	グラホ 1300	塩化物	500	転化
PPC056144A	20%Pt, 10%EtOH	グラホ 1322	塩化物	225	小ビーク
PPC056145A	20%Pt, 10%EtOH	グラホ 1300	塩化物	225	大部分
PPC056147A	20%Pt, エチレングリコール	グラホ 1322	アミン	300	一部
PPC056148A	20%Pt, エチレングリコール, PVP (10K)	グラホ 1322	アミン	300	一部
PPC056149A	20%Pt, エチレングリコール	グラホ 1300	アミン	300	一部
PPC056150A	20%Pt, エチレングリコール, PVP (10K)	グラホ 1300	アミン	300	一部
PPC056151A	20%Pt, エチレングリコール	グラホ 1300	塩化物	300	
PPC056152A	20%Pt, エチレングリコール	グラホ 1300	塩化物	300	転化
PPC056164A	20%Pt, 10%EtOH	グラホ 1300	アミン	521/28 9	

In the result of Table 23, alcohol, such as ethanol or a methanol, suggests making low only about 150 degrees C of conversion temperature of platinum, often distributing microcrystal.

[0427]

Thermogravimetric analysis (TGA) was performed using phosphorus SEISU (Linseis) (Model L81). It used for the sample preparation of all the amount measurement of metals and atomic absorption (AA) measurement of TGA, and a moisture content. During TGA measurement activation, it stops having burned, only a metal remains and carbon serves as an ideal start ingredient of AA analysis. The amount of the water in a catalyst is calculated from mass reduction of about 100 degrees C. This is important especially in analysis of the catalyst changed at low temperature.

[0428]

An atomic-absorption-spectroscopy method is used and he is PerkinElmer (Perkin-Elmer) AAnalyst. The quantum of the amount of the metal in a catalyst was carried out by 300. The catalyst was first heated by TGA and carbon support was removed. Next, the remaining metal nugget was dissolved in the aqua regia (3:1 HCl:HNO<sub>3</sub>). The obtained solution was diluted as required in order to consider as the concentration in the linearity field of equipment.

[Table 24]

表 2 4 . 原始吸光の結果概要

サンプル	Wt.%Pt 計算値	方法 1	方法 2	%
PPC056103A	5	5.7	--	--
PPC056104A	10	6.0	9.0	27.0 (フィルタ上に C が残存)
PPC056105A	20	13.9	16.4	36.8 (フィルタ上に C が残存)
PPC056096A	20	13.8*	18.8	32.4 (フィルタ上に C が残存)
PPC056106A	30	21.5	25.1	25.8 (フィルタに C は残っていない)
PPC056106A	40	33.8	--	--
PPC056102A	60	74.3	--	53.6 (フィルタ上に C が残存)
PPC056156A	20	--	16.8	44.0 (フィルタ上に C が残存)
PPC056158A	5	--	7.2	7.2 (フィルタ上に C が残存)

There was the residue of carbon in it, after heating a sample at 1300 degrees C, as shown in Table 24. Since carbon must have stopped having burned at 500 degrees C, I was not able to think that this was seemingly reasonable. It was consumed by the sample whose available oxygen in a sample chamber is about 5mg, and it turned out that the remaining samples were not able to burn while oxygen had been insufficient.

[0429]

Using the transmission electron microscope (TEM), platinum microcrystal size was measured and those distributions were investigated visually. Counting of the microcrystal was measured and carried out and drawing 80 and distribution of 81 and 82 were acquired. Since this technique has the assumption which can be seen that the microcrystal of an aggregated particle edge is typical, it is near evaluation of microcrystal size. Furthermore, it is difficult to lap with a big particle, to come out, and to include a very big particle, since the difference between a certain things is not always clear.

[0430]

The comparison with PPC056158B and PPC056159B illustrates contribution of high surface area carbon support. The microcrystal of sample PPC056158B (SHAWINIGAN BLACK (trademark)) is half magnitude mostly compared with the thing of PPC056159B (VULCAN(trademark) XC-72). VULCAN (trademark) The surface area of XC-72 is SHAWINIGAN. It is 3 times as large as that of BLACK (trademark), and average microcrystal size is about 2/3.

[0431]

It illustrates that distribution of platinum depends for these distribution on carbon support. As mentioned above, in the predetermined amount of platinum support, it is expected that the more often distributed catalyst should be acquired from the carbon support of high surface area. This can be easily grasped from drawing. VULCAN (trademark) The surface area of XC-72 is 240m<sup>2</sup>/g, and, on the other hand, is SHAWINIGAN. BLACK (trademark) is 80m<sup>2</sup>/g. At sample PPC056159B, platinum is SHAWINIGAN. It is 10wt(s)% on BLACK (trademark), and, on the other hand, is VULCAN (trademark) at PPC056158B. It is 10wt(s)% on XC-72.

Distribution of PPC056158B (average microcrystal size 1.8nm) is quite narrower than that of PPC056159B (average microcrystal size 3.0nm). 60% of difference in this microcrystal size supports the opinion that any same amounts of metal support are not the optimal for [ all ] carbon support.

[0432]

NAFION which supports the platinum of 0.2 mg/cm<sup>2</sup> to the cathode side where a work area has gas of atmospheric pressure for a hydrogen-air cel by 2 50cm (trademark) It formed by the film of 112.

[0433]

The engine performance as the whole MEA is given as a PRF, and this is the current density of potential 0.7V. The result of Table 25 will support the opinion are good, if distribution of platinum is made to maximize. The electrochemical engine performance of the catalyst prescribed with the platinum chloride is quite lower than the engine performance of the catalyst from a platinum amine. The difference in the microcrystal size evaluated by XRD was about 1/4 of the thing from a chloride with the catalyst based on an amine. These results suggest that better distribution is required, when it is going to use a platinum chloride as a precursor.

[Table 25]

表 25. PEMFC における Pt/C 電極触媒の電気化学的評価

サンプル	組成 (wt%)	カーボン支持体	前駆体	処理温度 (°C)	EC 活性 (mA/cm <sup>2</sup> )
PPC093109A	20%Pt	グラホ 1300	アミン	500	110, 38 alk
PPC093109B	20%Pt	グラホ 1300	アミン	600	35 alk 0.6V
PPC056087A	20%Pt	グラホ 1300	アミン	500	210
PPC056093A	20%Pt	グラホ 1300	アミン	475	作動せず
PPC056096A	20%Pt	グラホ 1300	アミン	500	190
PPC056101A	40%Pt	グラホ 1300	アミン	500	280
PPC056104A	10%Pt	グラホ 1300	アミン	500	120
PPC056105A	20%Pt	グラホ 1300	アミン	500	230
PPC056106A	30%Pt	グラホ 1300	アミン	500	120
PPC056142A	20%Pt	グラホ 1300	塩化物	350	10
PPC056143A	20%Pt	グラホ 1322	塩化物	500	180/190
PPC056144A	20%Pt, 10%EtOH	グラホ 1322	塩化物	225	75
PPC056156A	20%Pt	グラホ 1300	アミン	500	240
PPC056157A	20%Pt	グラホ 1322	アミン	482/244	240
PPC056157C	20%Pt	グラホ 1300	アミン	482/249	110
PPC056158B	10%Pt	グラホ 1322	アミン	517/265	180
PPC056159B	10%Pt	グラホ 1300	アミン	515/274	240
PPC056163C	20%Pt	グラホ 1300	アミン	526/282	120
PPC056164C	20%Pt	グラホ 1322	アミン	524/287	260

Since preparation of MEA required the great effort, some of catalysts of Table 25 were examined as alkaline cathode as an attempt to quick screening. Although a result cannot carry out a direct comparison with what was obtained from MEA, it is thought that relative activity is useful although catalytic activity is evaluated.

[0434]

The comparison of PPC056163C (SHAWINIGAN BLACK (trademark)) formed on the same spray drier conditions and PPC056164C (VULCAN(trademark) XC-72) illustrates contribution of the support to conversion temperature again. Therefore, the carbon support of high surface area should be used combining spray drier processing conditions.

[0435]

Sample PPC056156A is also the platinum support SHAWINIGAN. Although it is BLACK (trademark), electrochemical activity is a much appropriate value. By the comparison of PPC056159B and PPC056163C, it is thought that spray drier processing temperature is low-temperature threshold value for conversion of

platinum. In 10wt(s)% platinum, conversion is successful, and electrochemical activity is very good \*\*\*\*\*. However, 20wt% platinum shows that electrochemical activity is quite low and platinum will be in the same condition.

[0436]

It can be concluded that the particle is put to the temperature lower than the inside of an elevated-temperature wall surface reactor in a spray drier. this discovery -- SHAWINIGAN BLACK (trademark) -- VULCAN (trademark) although it suggests that temperature higher than XC-72 is required, this mechanism is a surface area dependency -- or it is not clear immediately whether it is based on the difference in the structure between carbon.

[0437]

Pt/C electrode catalyst [ of this invention ], conventional technique [ 10wt(s)% of ], and 20wt(s)% Pt/VULCAN (trademark) The comparison of Pt cluster size distribution between XC-72 was obtained from TEM data. This data is the same carbon support and VULCAN (trademark). By Pt concentration (XC-72 and 10wt(s)%),  $d_{av}=2.5\text{nm}$  average Pt microcrystal size was observed to the sample of the conventional technique, and, on the other hand,  $d_{av}=1.8\text{nm}$  was called for from the electrode catalyst of this invention. This result shows that the spraying generation method of this invention makes the electrode catalyst which Pt more often distributed, when the same support is used by the same Pt concentration.

[0438]

The property of the electrode catalyst of the conventional technique over the property which was excellent in the 20wt% electrode catalyst of this invention is illustrated by drawing 83 . The electrode catalyst of this invention is the same amount of Pt support, and shows about 50% of improvement to the electrode catalyst of the conventional technique. The electrode catalyst of this invention of said comparison is VULCAN (trademark) used with the electrode catalyst of the conventional technique. It is SHAWINIGAN to XC-72. It should be cautious of having been built with BLACK (trademark) support. SHAWINIGAN BLACK (trademark) support is VULCAN (trademark) which has quite small surface area, therefore has much big surface area. Compared with XC-72, it is more difficult to attain high distribution of Pt on this support.

[0439]

The result of the electrochemical trial to the latest 10 percentage-by-weight spray drier scale-up sample (on VULCAN(trademark) XC-72 and SHAWINIGAN BLACK (trademark) both support) shown in drawing 84 is almost equal to the engine performance which was excellent in the laboratory scale sample built using the supersonic wave. The latest 20wt% spray drier scale-up sample shown in drawing 85 , VULCAN (trademark) The result of the electrochemical trial to the sample prepared by XC-72 shows the engine performance which was excellent compared with the commercial sample of the 20wt% conventional technique (it excels about 40%).

[0440]

Next, the laboratory prototype MEA was built using these Pt/C electrode catalysts for the comparison with the existing marketing MEA. This MEA was examined in the independent experiment engine superintended by the fuel cell manufacturer. A target is the minimum possible amount of Pt support, and is completing MEA with the engine performance which fills the engine performance of about 600 mA/cm<sup>2</sup> with 0.6V. Since the amount of Pt support of the present marketing MEA is too high for prolonged commercialization, making the amount of Pt support low lengthens like the path to commercialization more.

[0441]

The comparison of the engine performance of MEA which includes a 20wt%Pt/C catalyst in the total amount of support of 0.25 mgPt/cm<sup>2</sup> to MEA of the conventional technique in which the total amount of Pt support is 0.8 mgPt/cm<sup>2</sup> is shown in drawing 86 . MEA including the catalyst of this invention is the basis of the conditions that Pt fewer than 1/3 is included, and this plot shows that two sorts of MEA(s) are similar engine performance.

[0442]

In order to show that this result is not limited to a specific sample or distribution of Pt, that use created another polarization curve which has 1 set of another engine-performance specifications. In this case, the 60wt%Pt/C sample was prepared and this was examined by MEA to Pt black (namely, 100%Pt) of a simple substance. By the low current consistency, the electrode catalyst containing fewer Pt of this invention was the comparable engine performance, and was the engine performance which was more excellent in high current density.

[0443]

Another point important about commercial application of these ingredients is a period when the engine performance is maintained. It can ask for this by recording either of the currents in the electrical potential difference or fixed electrical potential difference in a fixed current. Drawing 87 and 88 offer a certain information about change of the current density in the fixed electrical potential difference under the shown conditions.

[0444]

Thus, MEA made using the electrode catalyst of this invention showed the same engine performance by 0.25 mgPt/cm<sup>2</sup> to MEA of the conventional technique which is 0.8 mgPt/cm<sup>2</sup>.

[0445]

Pt-Pu/C and the Pt-Pd-Ru/C electrode catalyst for PEMFC anode plates The structure of the following two components and 3 component catalysts and the purpose of evaluation of a presentation are clarifying the processing conditions from which the catalyst which has the highest electrochemical activity is acquired. In addition to the electrode catalytic activity over oxidation reaction of hydrogen, a PEMFC anode plate catalyst must be CO resistance. The important point of this evaluation is asking for whenever [ between metals / alloying ]. The most important analysis information is acquired from XRD, TEM, and electrochemical evaluation.

[0446]

Table 26 enumerates produced 2 component catalyst Pt-Ru/C, and Table 27 enumerates produced 3 component catalyst Pt-Pd-Ru/C.

[Table 26]



表 26. Pt-Ru/C 電極触媒を調製するための実験条件

サンプル	組成 (wt. %)	カーボン支持体	前駆体	温度 (°C)
PPR056073A	20wt. %Pt/Ru 1:1	グラホ 1300	アミン/ニトロシル	500
PPR056074A	20wt. %Pt/Ru 1:1	グラホ 1300	アミン/ニトロシル	500
PPR056076A	20wt. %Pt/Ru 1:1	グラホ 1300	アミン/ニトロシル	400
PPR056077A	20wt. %Pt/Ru 1:1	グラホ 1300	水酸化物/ニトロシル	400
PPR056077E	20wt. %Pt/Ru 1:1	グラホ 1300	水酸化物/ニトロシル	250
PPR097110B	20%Pt/Ru, 1:1	グラホ 1301	アミン/ニトロシル	600F
PPR097111A	20%Pt/Ru, 1eq HCOOH	グラホ 1306	アミン/ニトロシル	600F
PPR097110C	20%Pt/Ru, 1eq HCOOH	グラホ 1307	アミン/ニトロシル	400F
PPR097111C	20%Pt/Ru, 4eq HCOOH	グラホ 1308	アミン/ニトロシル	600F
PPR097111B	20%Pt/Ru, 4eq HCOOH	グラホ 1309	アミン/ニトロシル	400F
PPR097126A	60%Pt/Ru, 1:1	グラホ 1300	アミン/ニトロシル	500
PPR093104E	20%Pt/Ru, 1:1	グラホ 1300	アミン/ニトロシル	550
PPC093105A	20%Pt/Rt, 1:1 NaBH <sub>4</sub>	グラホ 1300	アミン/ニトロシル	400
PPC093105B	20%Pt/Rt, 1:1 NaBH <sub>4</sub>	グラホ 1300	アミン/ニトロシル	350
PPR113014A	20%Pt/Rt, 1:1	グラホ 1300	塩化物	400F
PPR113014B	20%Pt/Rt, 1:1	グラホ 1300	塩化物	400F
PPR113014C	20%Pt/Rt, 1:1	グラホ 1300	塩化物	400F
PPR113015A	20%Pt/Rt, 1:1, KBH <sub>4</sub>	グラホ 1300	塩化物	400F
PPR113015B	20%Pt/Rt, 1:1, 尿素	グラホ 1300	塩化物	400F
PPR093109C	20%Pt/Rt, 1:1	グラホ 1300	アミン/ニトレート	600
PPR093109D	20%Pt/Rt, 1:1	グラホ 1300	アミン/ニトレート	500
PPR056088A	20%Pt/Rt, 1:1	グラホ 1300	アミン/ニトレート	500

[Table 27]

表 27. Pt/Ru/Pd 電極触媒を調整するための実験条件

サンプル	組成 (wt. %)	カーボン支持体	前駆体	温度 (°C)
PPC113015C	20%Pt/Pd/Ru, 30:30:40	グラホ 1300	塩化物	400F
PPC113016A	20%Pt/Pd/Ru, 30:30:40	グラホ 1300	塩化物	400F
PPC113017A	20%Pt/Pd/Ru, 40:40:20	グラホ 1300	塩化物	400F
PPC113017B	20%Pt/Pd/Ru, 40:40:20	グラホ 1300	塩化物	400F
PPC113016B	20%Pt/Pd/Ru, 30:30:40, KBH <sub>4</sub>	グラホ 1300	塩化物	400F
PPC113017C	20%Pt/Pd/Ru, 40:40:20, KBH <sub>4</sub>	グラホ 1300	塩化物	400F
PPC113016C	20%Pt/Pd/Ru, 30:30:40, 尿素	グラホ 1300	塩化物	400F
PPC113018A	20%Pt/Pd/Ru, 40:40:20, 尿素	グラホ 1300	塩化物	400F
PPP093105C	20%Pt/Pd/Ru, 30:30:40	グラホ 1300	アミン/ニトレート	500
PPP093105D	20%Pt/Pd/Ru, 30:30:40	グラホ 1300	アミン/ニトレート	550
PPP093105E	20%Pt/Pd/Ru, 30:30:40	グラホ 1300	アミン/ニトレート	600
PPP093105F	20%Pt/Pd/Ru, 30:30:40	グラホ 1300	アミン/ニトレート	650
PPP093105G	20%Pt/Pd/Ru, 30:30:40	グラホ 1300	アミン/ニトレート	700
PPP093106A	20%Pt/Pd/Ru, 40:40:20	グラホ 1300	アミン/ニトレート	500
PPP093106B	20%Pt/Pd/Ru, 40:40:20	グラホ 1300	アミン/ニトレート	550
PPP093106C	20%Pt/Pd/Ru, 40:40:20	グラホ 1300	アミン/ニトレート	600
PPP093106D	20%Pt/Pd/Ru, 40:40:20	グラホ 1300	アミン/ニトレート	650
PPP093106E	20%Pt/Pd/Ru, 40:40:20	グラホ 1300	アミン/ニトレート	700
PPP093107A	20%Pt/Pd/Ru, 40:40:20	グラホ 1300	アミン/ニトレート	400
PPP093107B	20%Pt/Pd/Ru, 40:40:20	グラホ 1300	アミン/ニトレート	500

PPP093109E	20%Pt/Pd/Ru, 30:30:40	グラホ 1300	アミン/ニトレート	500
PPP093109F	20%Pt/Pd/Ru, 30:30:40	グラホ 1300	アミン/ニトレート	600
PPP093109G	20%Pt/Pd/Ru, 40:40:20	グラホ 1300	アミン/ニトレート	600
PPP093109H	20%Pt/Pd/Ru, 40:40:20	グラホ 1300	アミン/ニトレート	500
PPP056089A	20%Pt/Pd/Ru, 30:30:40	グラホ 1300	アミン/ニトレート	500
PPP056090A	20%Pt/Pd/Ru, 40:40:20	グラホ 1300	アミン/ニトレート	500

The XRD spectrum showed the peak which corresponds to Pt-Ru and shows metaled alloying. Since the both sides of palladium and platinum melt into an aqua regia, analysis of palladium resembles analysis of platinum. The elemental analysis of a ruthenium content catalyst is not simple. After removing carbon by TGA, a sample can be analyzed by the two roots. using the easy dissolution to an aqua regia, the platinum (case where it exists again -- palladium) content of a sample can be calculated, and then a ruthenium content can be calculated as a difference. More, by heating with a sodium peroxide, sodium fusion of the sample may be carried out to accuracy, and then you may leach with an aqua regia to it. Next, atomic absorption can analyze the obtained solution.

[0447]

Pt-Ru/C of this invention and the relative electrochemistry activity of a Pt-Ru-Pd/C catalyst were investigated. The catalyst was pressed in the electrode and it evaluated as a barrier layer of 20 mg/cm<sup>2</sup> which has the gaseous diffusion layer of 50 mg/cm<sup>2</sup> XC-35 among 7-N KOH.

[Table 28]

表 28. Pt-Ru/C 及び Pt-Ru-Pd/C 触媒の電気化学的評価データ

サンプル	組成	温度 (°C)	PRF in 7N KOH
PPR093109C	PtRu	600	25
PPR093109D	PtRu	500	18
PPR093109E	PtPdRu	500	35
PPR093109F	PtPdRu	600	30

Addition of palladium made the electrochemical activity of a catalyst increase considerably, as shown in Table 28. A similar catalyst and PPC093106A were put into MEA, and were built, and it examined by reformat (reformat). The test result in reformat is shown in the polarization curve of drawing 89.

[0448]

Drawing 89 compares the electrochemical activity of PPC093106A by both pure hydrogen and reformat. Since the polarization curve has almost lapped, CO resistance which was excellent in this catalyst can be known. This Pt-Pd-Ru catalyst functions by reformat almost the same with functioning from pure hydrogen.

In this way, Pt-Ru/C and a Pt-Ru-Pd/C electrode catalyst were used, and the outstanding engine performance under existence of CO of small concentration and low-concentration hydrogen was shown.

[0449]

Polymer qualification particle Together with the impermeability over a water solution, the greatest gas transparency must be possible for the gaseous diffusion layer (GDL) of the power unit of arbitration. There are various methods of obtaining a gaseous diffusion layer. According to an application, this layer is composite material, such as continuous fluorocarbon polymer film, carbon black by which hydrophobing was carried out, or a metallic oxide by which hydrophobing was carried out, etc., and it deals in it. A hydrophobic layer must be arranged with the structure of being suitable for making the layer which has the channel and hydrophobic pore of the optimal magnitude which active species can move, preventing an electrolyte oozing out. Furthermore,

hydrophobic pore must prevent a surrounding steam invading into a power unit. By changing the rate of a base material and a hydrophobic component, hydrophobic control of a hydrophobic layer can be performed by giving inclination to/or a hydrophobic layer again. The hydrophobing powder complex (polymer qualification carbon) manufactured by Table 29 according to this invention is packed.

[0450]

SHAWINIGAN whose fluorocarbon polymers are various rates of 5 - 60% of the weight of the range Shearing mixing of the dispersing element of various carbon, such as BLACK (trademark) and PWA, was carried out. Next, as shown in Table 29, spray drying of the dispersing element was carried out at various temperature. The dispersing element of metallic oxides, such as SiO<sub>2</sub>, aluminum 2O<sub>3</sub>, and TiO<sub>2</sub>, was prepared using the surfactant. In order to prevent foaming a fluorocarbon polymer dispersing element under existence of a surfactant, shearing mixing was carried out to the metallic-oxide dispersing element by low-power output. Next, spray drying of the dispersing element was carried out.

[0451]

The surface area and pore volume of the last powder were measured by nitrogen adsorption-desorption technique. The surface area of the last complex is called for with the surface area of hydrophobing carbon or a metallic oxide.

[Table 29]

表 29. ポリマー修飾粉末組成

サブストレート	温度	テフロン	S. A.	細孔体積	平均細孔直径
	(° F)	(wt. %)	(m <sub>2</sub> /g)	(cm <sub>3</sub> /g)	(nm)
SHAWINIGAN BLACK (R)	400	5	33	0.1384	16.8
SHAWINIGAN BLACK (R)	600	5	30.3	0.1361	18
SHAWINIGAN BLACK (R)	400	35	28.5	0.11	15.4
SHAWINIGAN BLACK (R)	600	35	27	0.1294	19.2
シリカ	600	60	81	0.614	30.3
SHAWINIGAN BLACK (R)	640	50	31.6	0.0843	10.6
SHAWINIGAN BLACK (R)	610	50	23	0.11	18.9
SHAWINIGAN BLACK (R)	640	35	101	0.13	5
SHAWINIGAN BLACK (R)	600	35			
PWA	615	50	226	0.17	3
PWA	600	50			
PWA	630	35	352	0.22	2.5
PWA	600	35			
Al <sub>2</sub> O <sub>3</sub>	600	50			
Al <sub>2</sub> O <sub>3</sub>	600	35			
TiO <sub>2</sub>	600	50			
TiO <sub>2</sub>	600	35			
TiO <sub>2</sub> (疎水性)	600	50	19.9	0.0747	14.9
TiO <sub>2</sub> (疎水性)	600	35			

Next, it carried out after treatment of the polymer qualification carbon complex for 15 minutes at 300 degrees C in order to burn a certain existing surfactant or binder, since a surfactant affects the engine performance of a gaseous diffusion layer. Polymer qualification carbon was pressed in the gaseous diffusion layer with the MnOx/C catalyst, and was measured electrochemically. Similarly, the polymer qualification carbon black from another source was pressed in the gaseous diffusion layer with the same catalyst, and it compared with the electrochemical engine performance of the polymer qualification carbon black of this invention.

[0452]

Drawing 90 is the polarization curve plotted to the polymer qualification carbon black prepared with various sources. Especially the polymer qualification carbon by this invention more often functions in oxygen and air with the current density of 100mA/cm<sup>2</sup> to which a limit of transportation and diffusion becomes dominant so that a polarization curve may show. This is still clearer from drawing 91, and this is the delta E plot of the difference in the engine performance in air and oxygen. It proves that the difference between the inside of oxygen and air is very small with the polymer qualification carbon of this invention, and the gaseous diffusion layer in which this was prepared using the polymer qualification carbon of this invention is the more excellent engine performance.

[0453]

By approaches, such as distribution (syringe dispensing), screen-stencil, etc. by the syringe, if these ingredients are printed more thinly, the thickness of a gaseous diffusion layer can be decreased further. The polymer qualification carbon compound was prepared by isopropanol by the alpha-terpineol again in order to make the film which raises further transportation of a polarization curve, and the engine performance of the part governed by diffusion adhere.

[0454]

Hydrophobing of the "Teflon-ized (TEFLONIZED)" black is carried out, and it uses carbon and the sprayed fluorocarbon polymer (TEFLON (trademark)). Similar complex can be manufactured for various applications, such as making easy transportation of chemical species to a catalyst site. The polymer distributed on a base material for a specific application can be chosen. For example, in order to make easy transportation of the proton to the NAFION (trademark) film, polymer qualification NAFION (trademark) carbon was prepared. About a NAFION (trademark) solution, it is VULCAN (trademark). XC-72 and SHAWINIGAN It mixed with various carbon dispersing elements of BLACK (trademark), and spray drying was carried out at 204 degrees C (400 degrees F). Table 30 packs these polymer qualification ingredients.

[Table 30]

表 30. ポリマー修飾粉末

生成 #PNF	組成 (wt. %) NAFION(R)	カーボン支持 体	SA (M <sup>2</sup> /g)	細孔体 積	平均細 孔直径	PSD d90 ミクロ ン
056129B	15	VULCAN(R) XC-32	71.36	0.262	14.7	19
056129C	10	VULCAN(R) XC-32	76.8	0.284	14.8	0.7
056130A	5	VULCAN(R) XC-32	86.43	0.334	15.46	0.8
056130C	15	SHAWINIGAN BLACK (R)	36.97	0.171	18.51	1.2
056131A	10	SHAWINIGAN BLACK (R)	36.96	0.167	18.06	1.2
056131B	5	SHAWINIGAN BLACK (R)	37.8	0.174	18.4	1.5

Drawing 92 and drawing 93 are the polymer qualification carbon by this invention, and SHAWINIGAN especially embellished with 5wt(s)% NAFION (trademark). It is the SEM microphotography of BLACK

(trademark).

In addition, in an accompanying drawing, cm<sup>2</sup> shall express cm<sup>2</sup> (square centimeter), and m<sup>2</sup> shall express m<sup>2</sup> (square meter).

[Brief Description of the Drawings]

[Drawing 1] Drawing showing the generation process of the electrode catalyst particle by the operation gestalt of this invention.

[Drawing 2] Drawing showing a useful NI hydraulic nozzle in manufacture of the electrode catalyst powder by the operation gestalt of this invention.

[Drawing 3] Drawing showing a useful spray drier in manufacture of the electrode catalyst powder by the operation gestalt of this invention.

[Drawing 4] Drawing showing a useful hybrid perpendicular reactor system in the spraying conversion for the particle formation by the operation gestalt of this invention.

[Drawing 5 a] Drawing showing this invention \*\*\*\* direct writing deposition method.

[Drawing 5 b] Drawing showing this invention \*\*\*\* direct writing deposition method.

[Drawing 6] Drawing showing the three-phase-circuit interface of energy devices, such as a cell or a fuel cell.

[Drawing 7] Drawing showing the air cathode by the operation gestalt of this invention.

[Drawing 8] Drawing showing the air cathode by another operation gestalt of this invention.

[Drawing 9] Drawing showing the air cathode by another operation gestalt of this invention.

[Drawing 10] Drawing showing the air cathode by another operation gestalt of this invention.

[Drawing 11] Drawing showing the air cathode by another operation gestalt of this invention.

[Drawing 12] Drawing showing the air cathode containing two or more monolayers which constitute an electrode by the operation gestalt of this invention.

[Drawing 13 a] Drawing showing the inclusion of a carbon-dioxide reduction zone to the air cathode by this invention.

[Drawing 13 b] Drawing showing the inclusion of a carbon-dioxide reduction zone to the air cathode by this invention.

[Drawing 14 a] Drawing showing the zinc air battery by the operation gestalt of this invention.

[Drawing 14 b] Drawing showing the zinc air battery by the operation gestalt of this invention.

[Drawing 15] Drawing showing the metal/air cell by the operation gestalt of this invention.

[Drawing 16] Drawing showing the metal/air cell by the operation gestalt of this invention.

[Drawing 17] Drawing showing roughly the membrane electrode assembly by the operation gestalt of this invention.

[Drawing 18] Drawing showing a membrane electrode assembly.

[Drawing 19] Drawing showing a polarization curve.

[Drawing 20] Drawing showing a polarization curve.

[Drawing 21] Drawing showing a polarization curve.

[Drawing 22] Drawing showing the barrier layer of various thickness.

[Drawing 23] Drawing showing a polarization curve.

[Drawing 24] Drawing showing a polarization curve.

[Drawing 25] Drawing showing a polarization curve.

[Drawing 26] Drawing showing a particulate structure.

[Drawing 27] Drawing showing layer structure.

[Drawing 28] Drawing showing a particulate structure.

[Drawing 29] Drawing showing a particulate structure.

[Drawing 30] Drawing showing a particulate structure.

[Drawing 31] Drawing showing the SEM microphotography of the electrode catalyst powder generated with the supersonic wave by the operation gestalt of this invention.

[Drawing 32] Drawing showing the particle size distribution of the electrode catalyst powder generated with the supersonic wave by the operation gestalt of this invention.

[Drawing 33] Drawing showing the particle size distribution of the electrode catalyst powder generated with the supersonic wave by the operation gestalt of this invention.

[Drawing 34] Drawing showing the particle size distribution of the electrode catalyst powder by spray drying by



the operation gestalt of this invention.

[Drawing 35] Drawing showing the MnOx cluster size dependency of the electrode catalytic activity in the electrode catalyst powder by the operation gestalt of this invention.

[Drawing 36] Drawing showing the relative intensity dependency of a XPS peak of the electrode catalytic activity in the electrode catalyst powder by the operation gestalt of this invention.

[Drawing 37] Drawing showing the effectiveness to the surface area by increasing the manganese concentration in the high surface area electrode catalyst powder by the operation gestalt of this invention.

[Drawing 38] Drawing showing the effectiveness to the surface area by increasing the manganese concentration in the high surface area electrode catalyst powder by the operation gestalt of this invention.

[Drawing 39] Drawing showing the effectiveness of manganese concentration over distribution of the active species on the high surface area electrode catalyst powder by the operation gestalt of this invention.

[Drawing 40] Drawing showing the effectiveness of manganese concentration over distribution of the active species on the high surface area electrode catalyst powder by the operation gestalt of this invention.

[Drawing 41] Drawing showing the effectiveness of the amount of MnOx support of an electrode catalyst particle.

[Drawing 42] Drawing showing the effectiveness of the amount of MnOx support of an electrode catalyst particle.

[Drawing 43] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 44] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 45] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 46] Drawing showing the effectiveness of reactor temperature over surface area.

[Drawing 47] Drawing showing the effectiveness of reactor temperature over surface area.

[Drawing 48] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 49] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 50] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 51] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 52] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 53] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 54] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 55] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 56] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 57] Drawing showing the polarization curve which shows the property of the membrane electrode assembly by this invention.

[Drawing 58] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 59] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 60] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 61] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 62] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 63] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 64] Drawing showing surface area as a function of spraying conversion temperature.

[Drawing 65] Drawing showing binding energy as a function of surface area.

[Drawing 66] Drawing showing XPS relative intensity as a function of conversion temperature.

[Drawing 67] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 68] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 69] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 70] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 71] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 72] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 73] Drawing showing the property of the membrane electrode assembly by this invention.

[Drawing 74] Drawing showing surface area as a function of the amount of platinum support.

[Drawing 75] Drawing showing surface area as a function of temperature.

[Drawing 76] Drawing showing the diameter of a platinum crystal at the time of being measured by FWHM of

a XRD pattern.

[Drawing 77] Drawing showing FWHM as a function of a platinum fill.

[Drawing 78] Drawing showing FWHM as a function of conversion temperature.

[Drawing 79] Drawing showing the TEM microphotography of the electrode catalyst powder by the operation gestalt of this invention.

[Drawing 80] Drawing showing the average microcrystal size of a Pt/C electrode catalyst.

[Drawing 81] Drawing showing the average microcrystal size of a Pt/C electrode catalyst.

[Drawing 82] Drawing showing the average microcrystal size of a Pt/C electrode catalyst.

[Drawing 84] Drawing showing the engine performance of the membrane electrode assembly by the operation gestalt of this invention.

[Drawing 85] Drawing showing the engine performance of the membrane electrode assembly by the operation gestalt of this invention.

[Drawing 86] Drawing showing the engine performance of the membrane electrode assembly by the operation gestalt of this invention.

[Drawing 87] Drawing showing the engine performance of the membrane electrode assembly by the operation gestalt of this invention.

[Drawing 88] Drawing showing the engine performance of the membrane electrode assembly by the operation gestalt of this invention.

[Drawing 89] Drawing showing the engine performance of the membrane electrode assembly by the operation gestalt of this invention.

[Drawing 90] Drawing showing the engine performance of the membrane electrode assembly by the operation gestalt of this invention.

[Drawing 91] Drawing showing the engine performance of the membrane electrode assembly by the operation gestalt of this invention.

[Drawing 92] The SEM microphotography of the polymer qualification particle by this invention.

[Drawing 93] The SEM microphotography of the polymer qualification particle by this invention.

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[Translation done.]

\* NOTICES \*

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

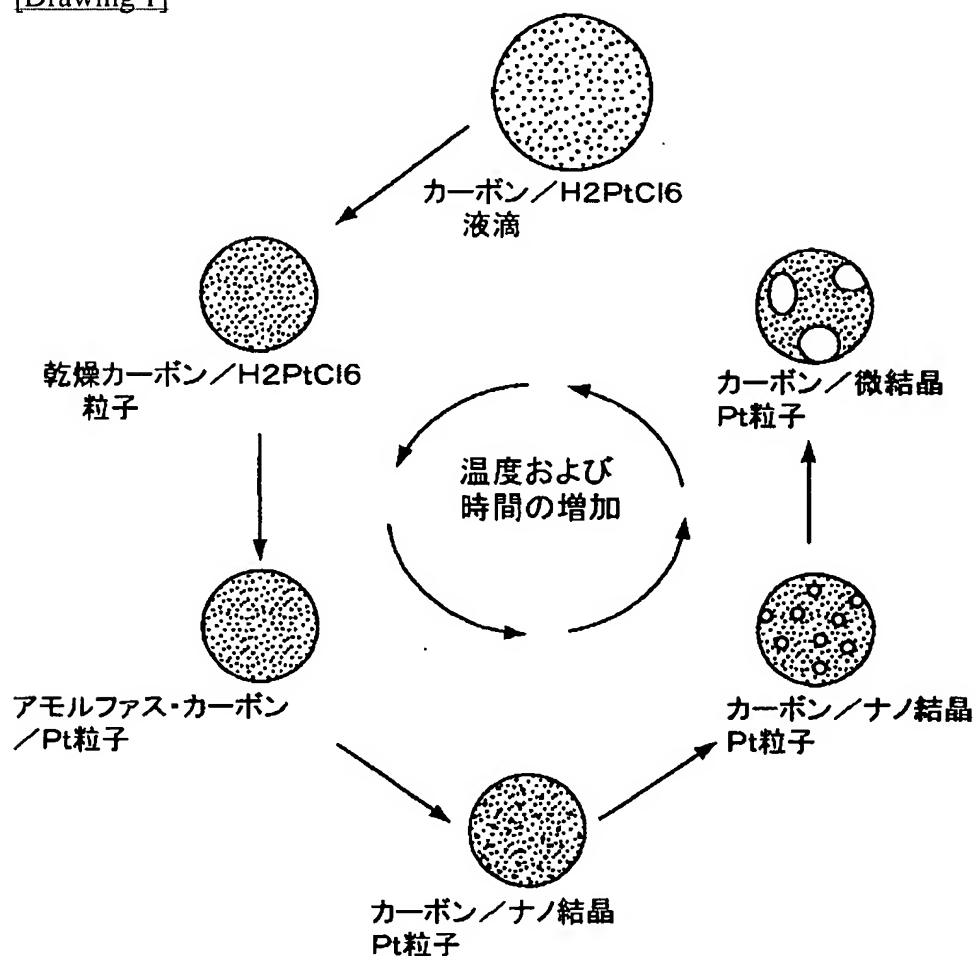
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2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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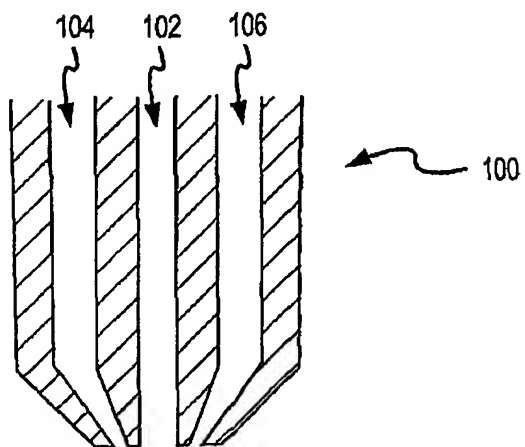
DRAWINGS

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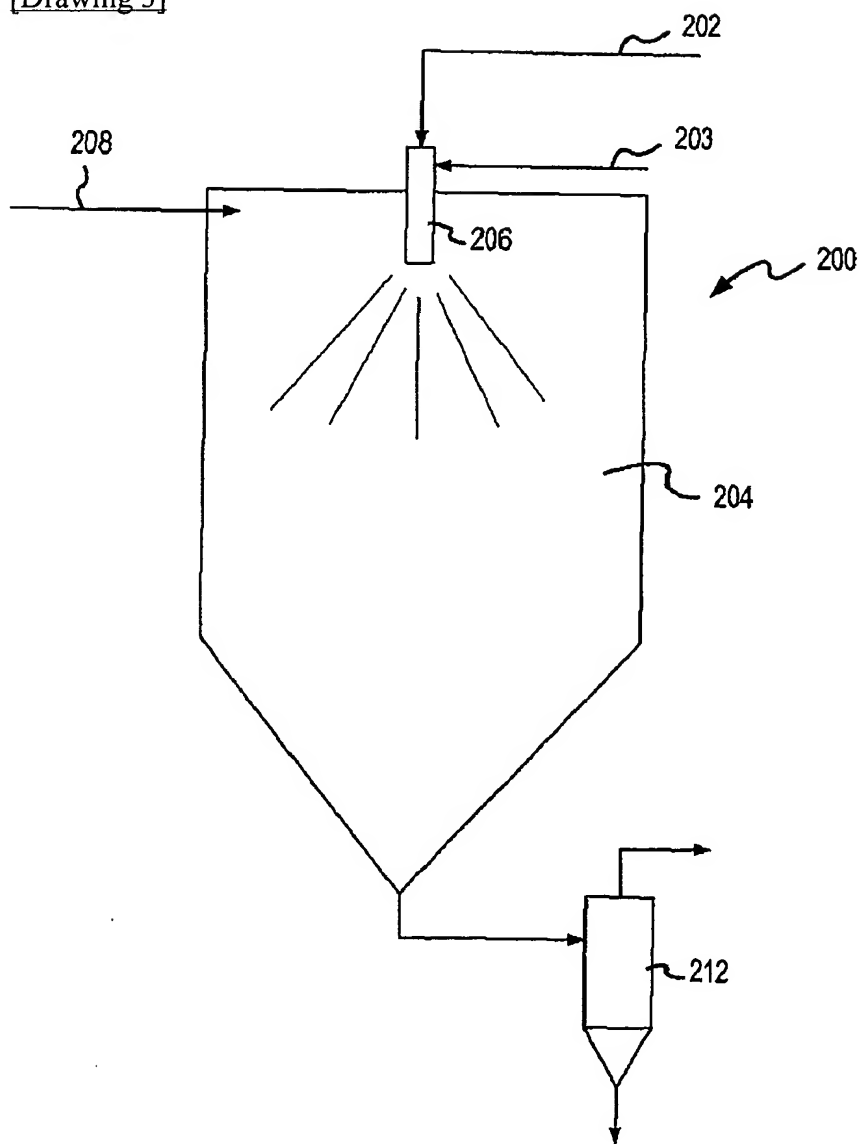
[Drawing 1]

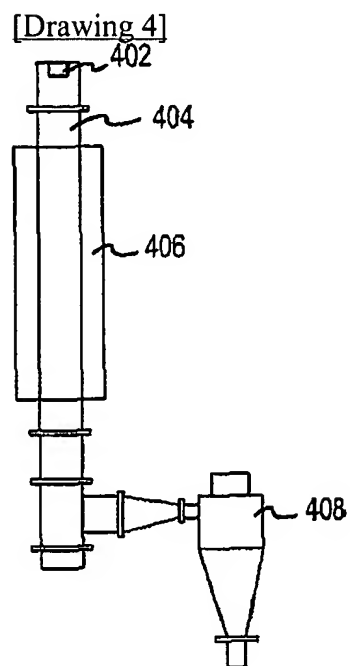
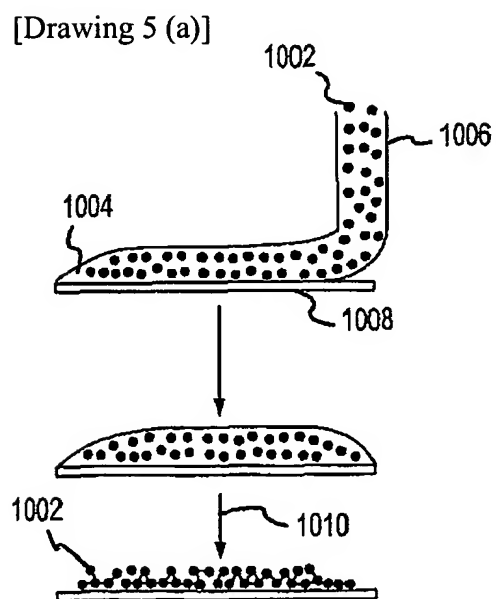


[Drawing 2]

**FIG. 2**

[Drawing 3]

**FIG. 3**

**FIG.4****FIG.5(a)**

[Drawing 5 (b)]

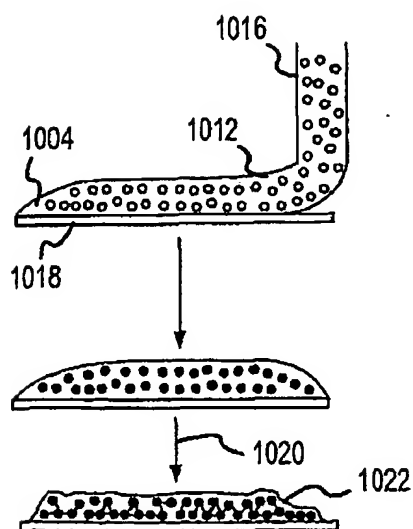


FIG.5(b)

[Drawing 6]

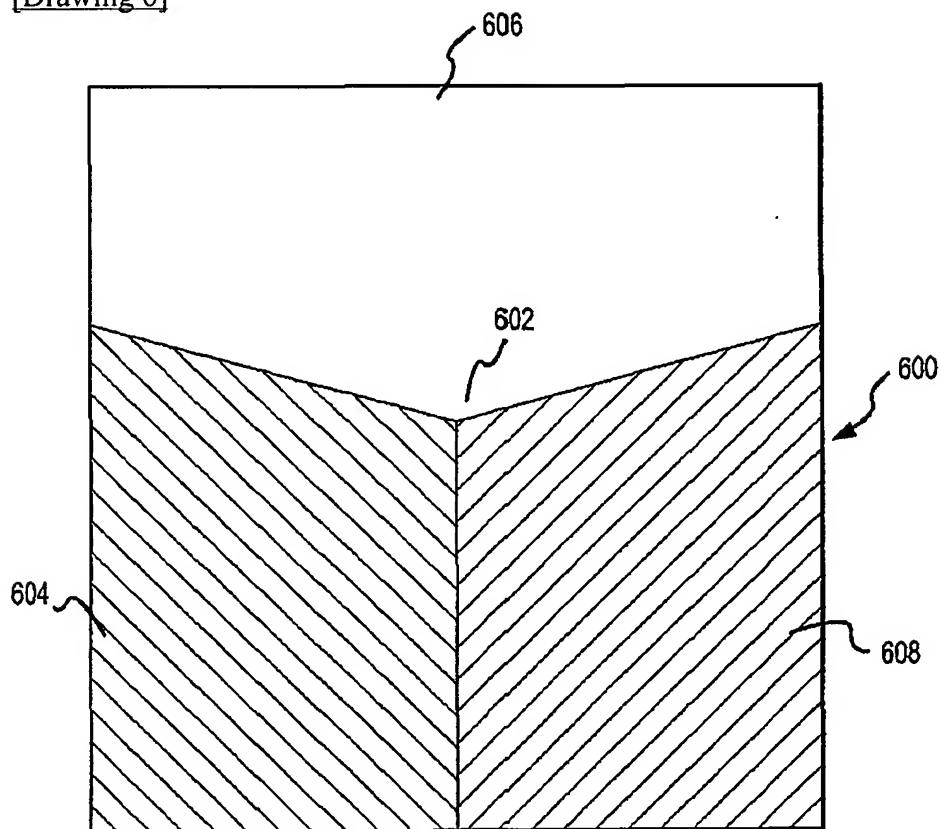


FIG.6

[Drawing 7]



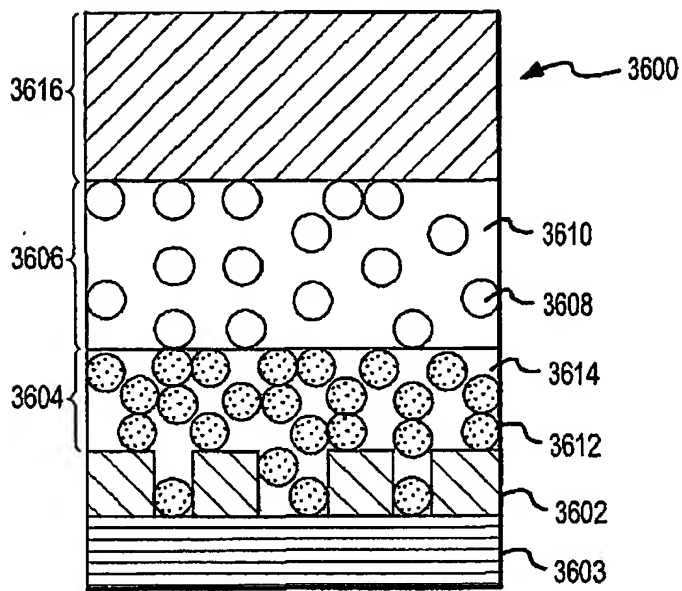


FIG.7

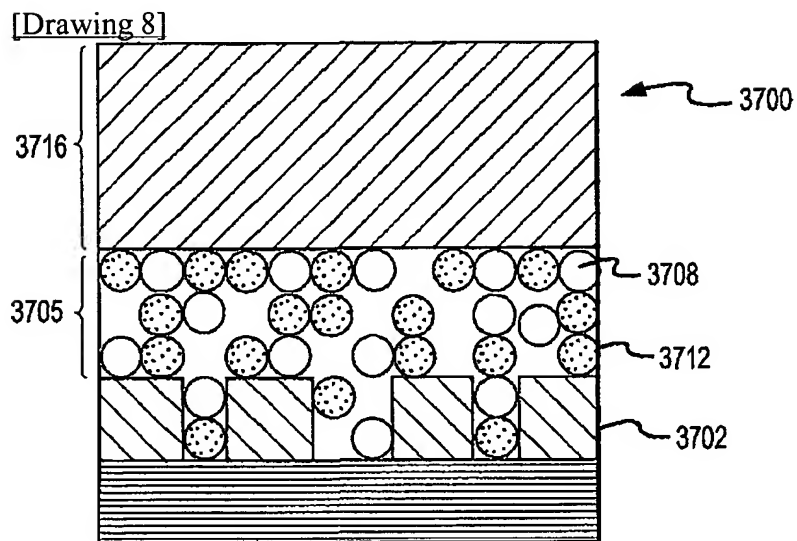


FIG.8

[Drawing 9]

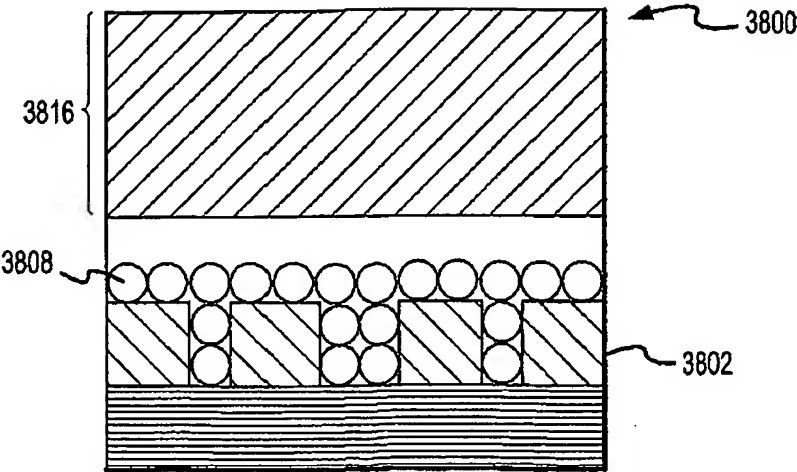


FIG.9

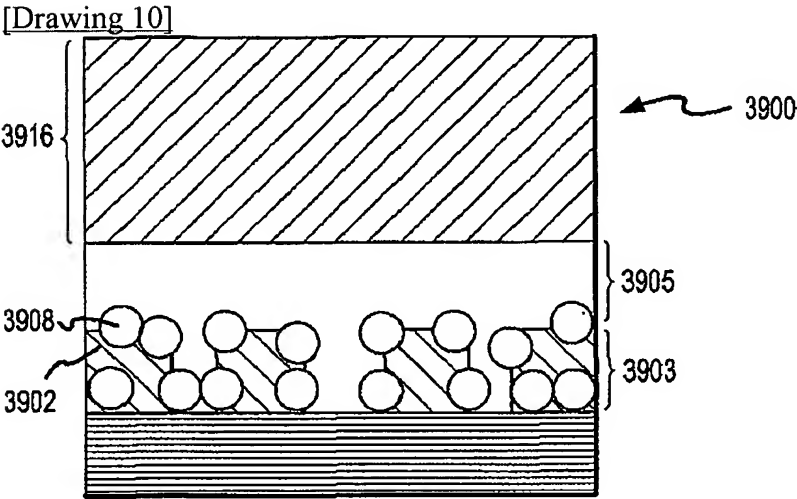


FIG.10

[Drawing 11]

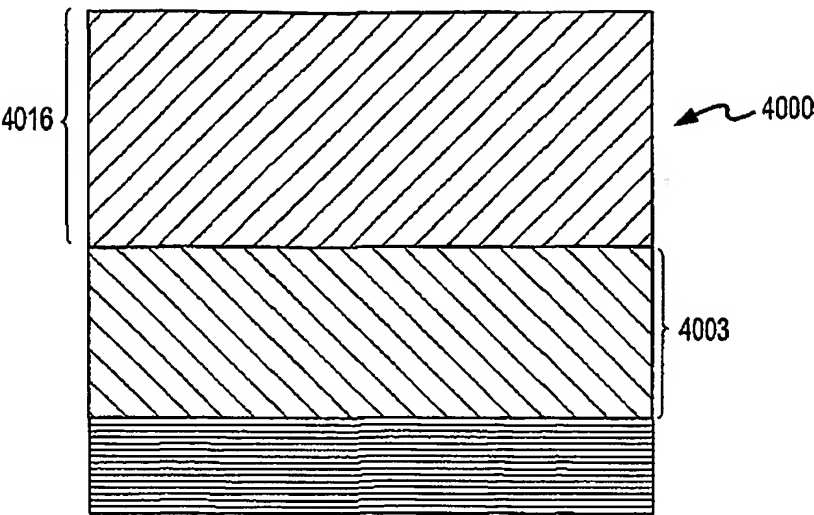


FIG.11

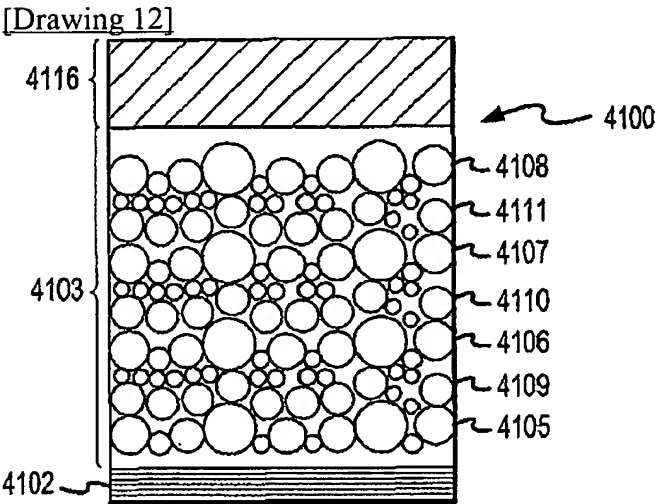


FIG.12

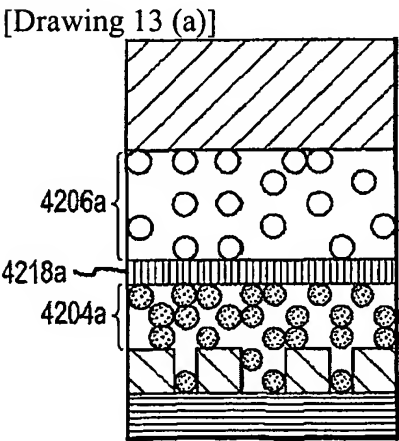


FIG.13(a)

[Drawing 13 (b)]

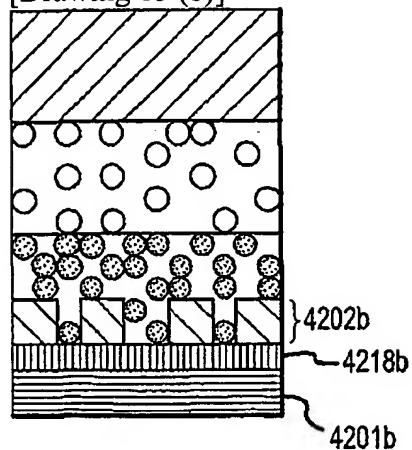


FIG.13(b)

[Drawing 14 (a)]

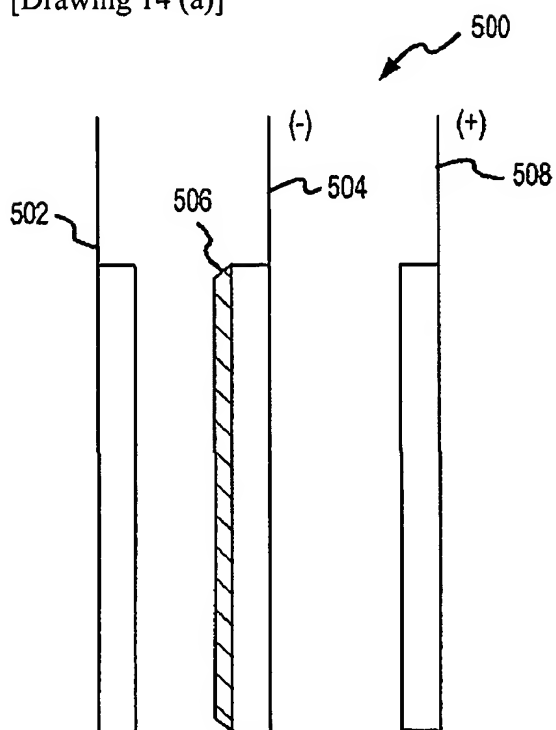


FIG.14(a)

[Drawing 14 (b)]

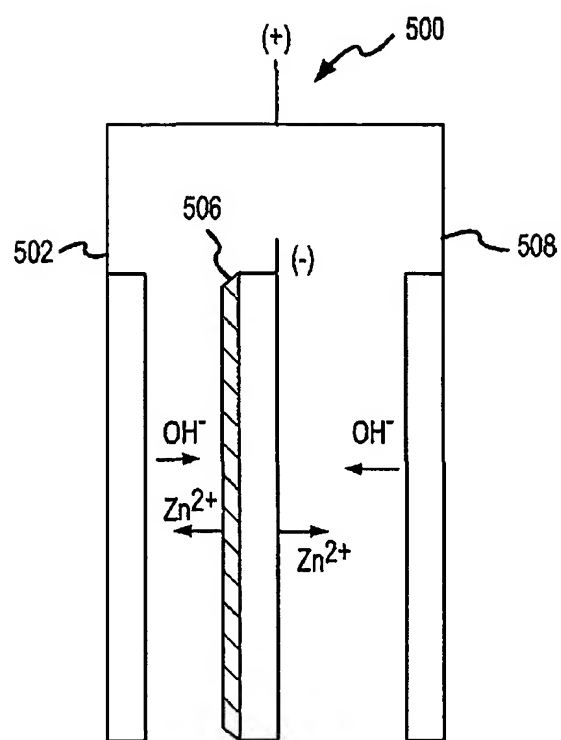
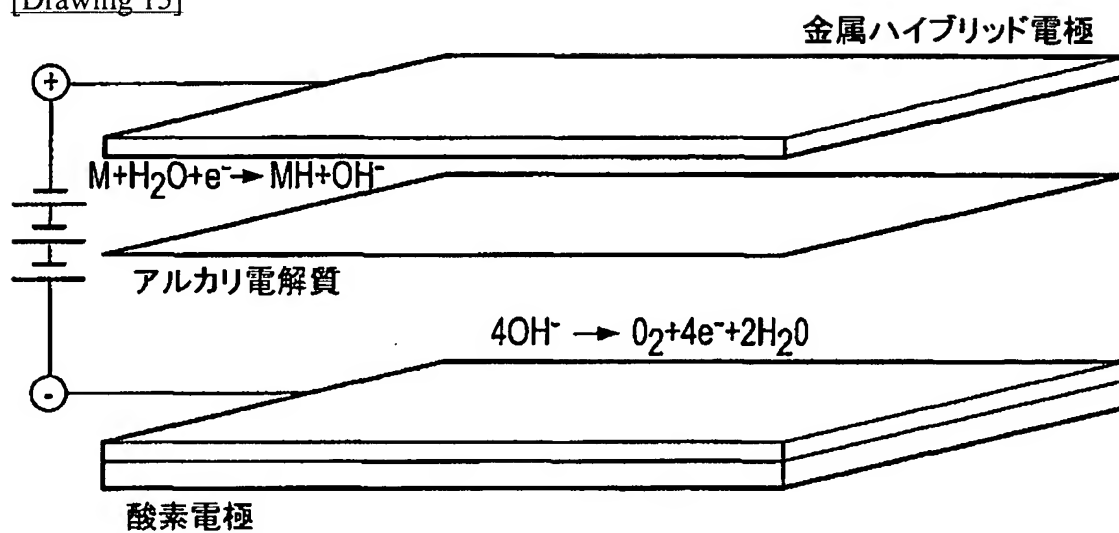
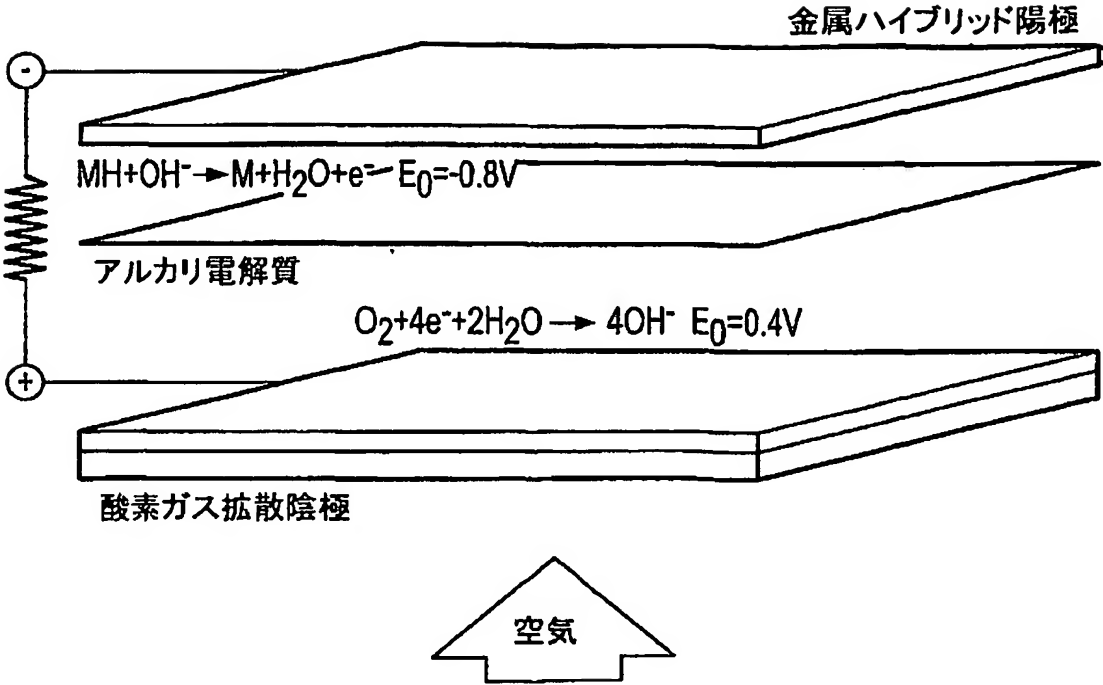


FIG. 14(b)

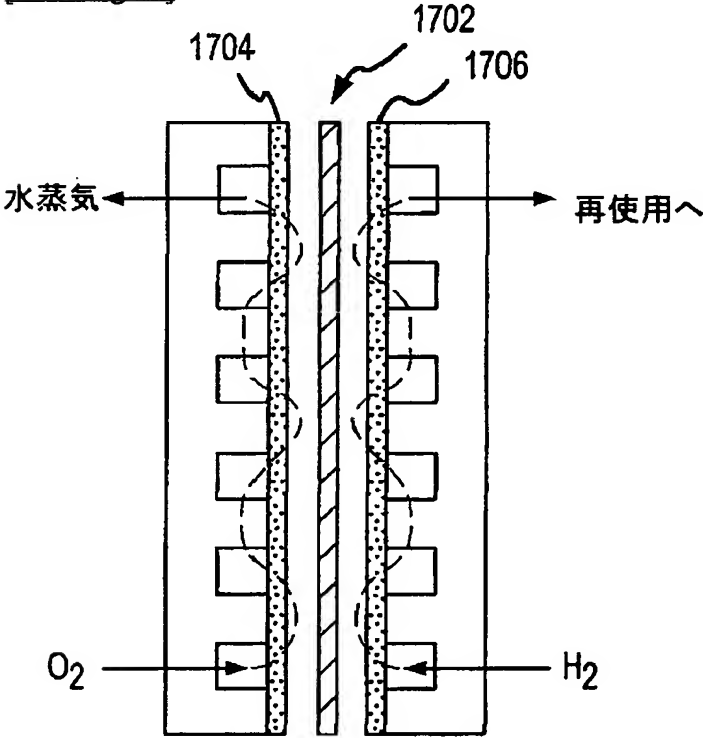
[Drawing 15]



[Drawing 16]

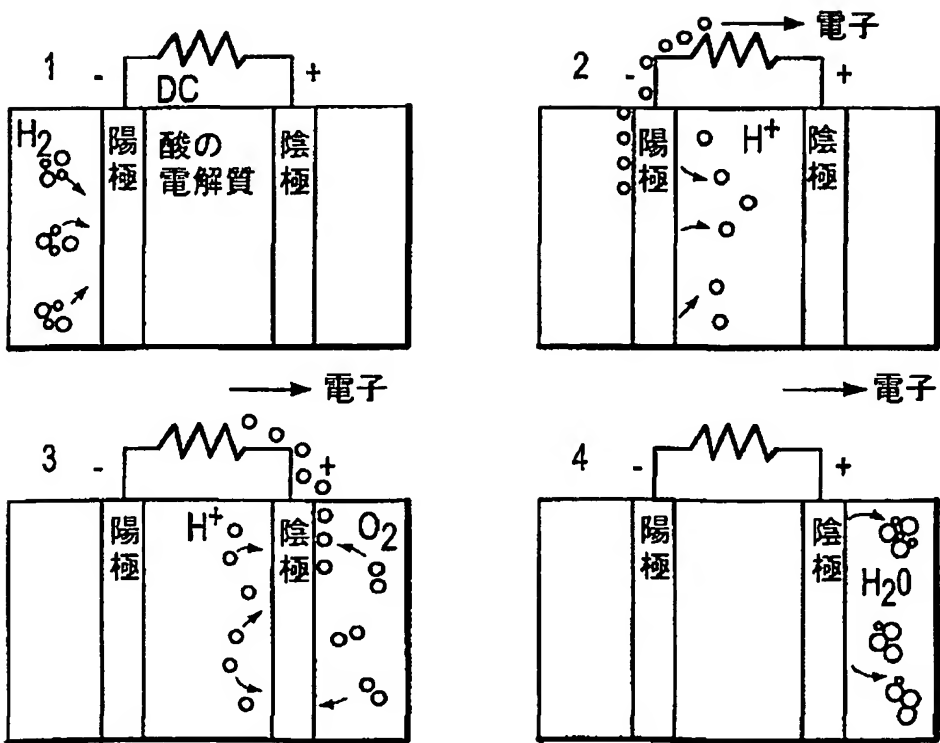


[Drawing 17]

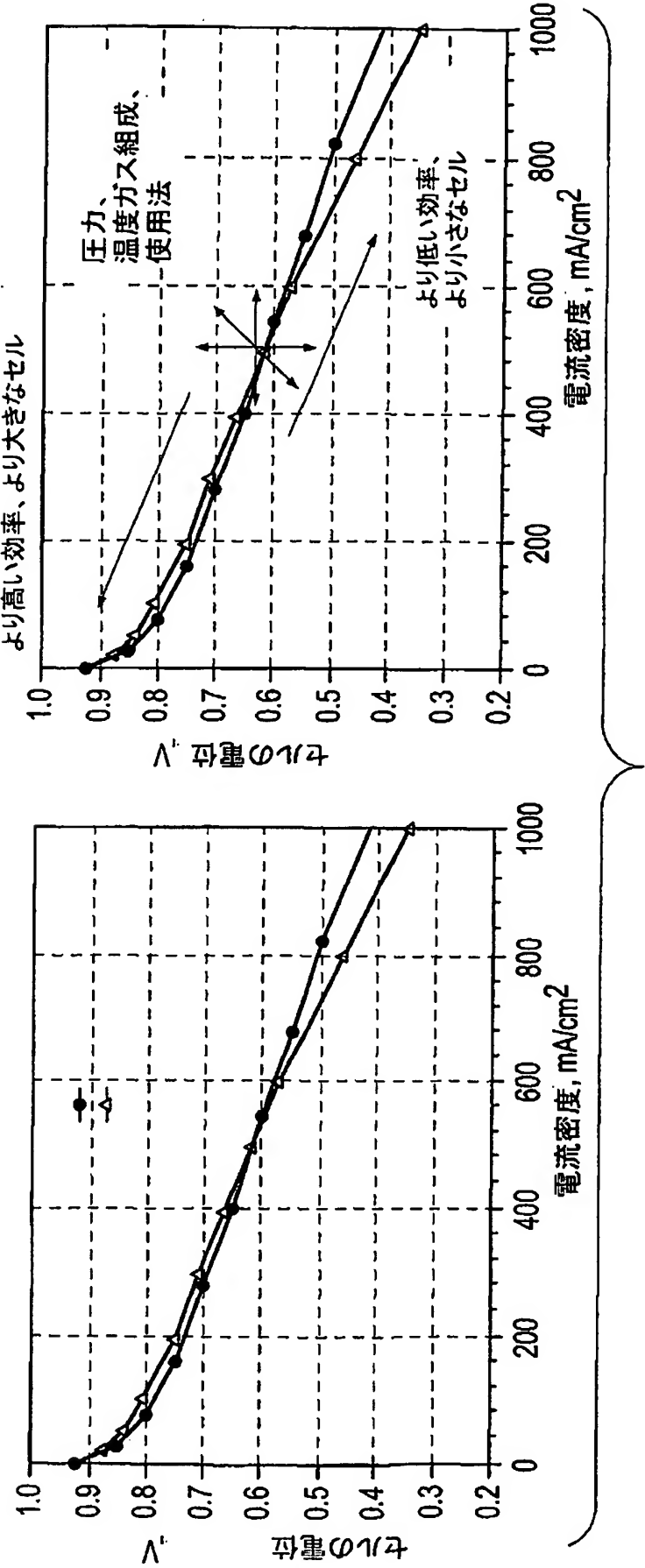


[Drawing 18]

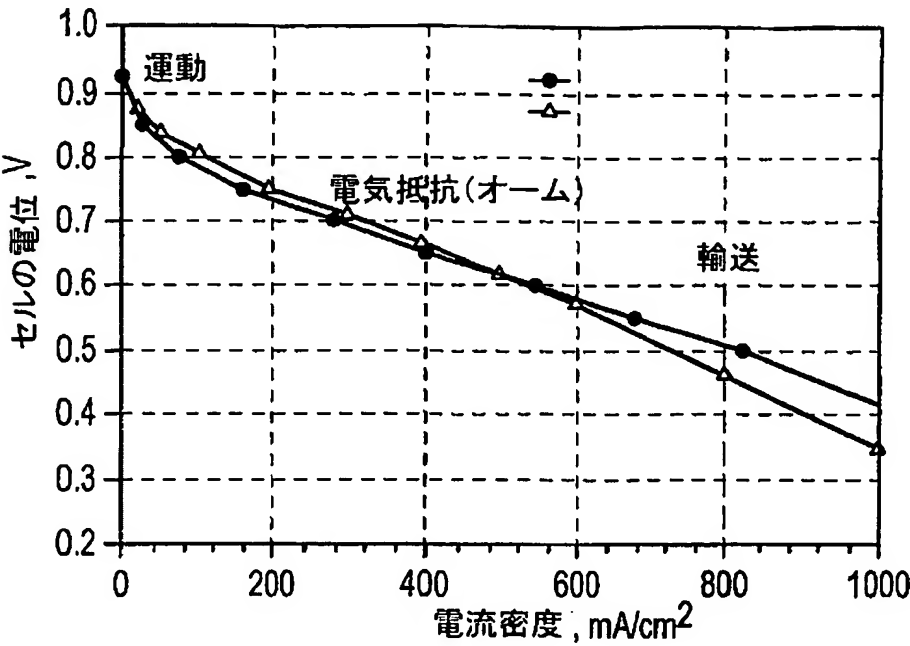




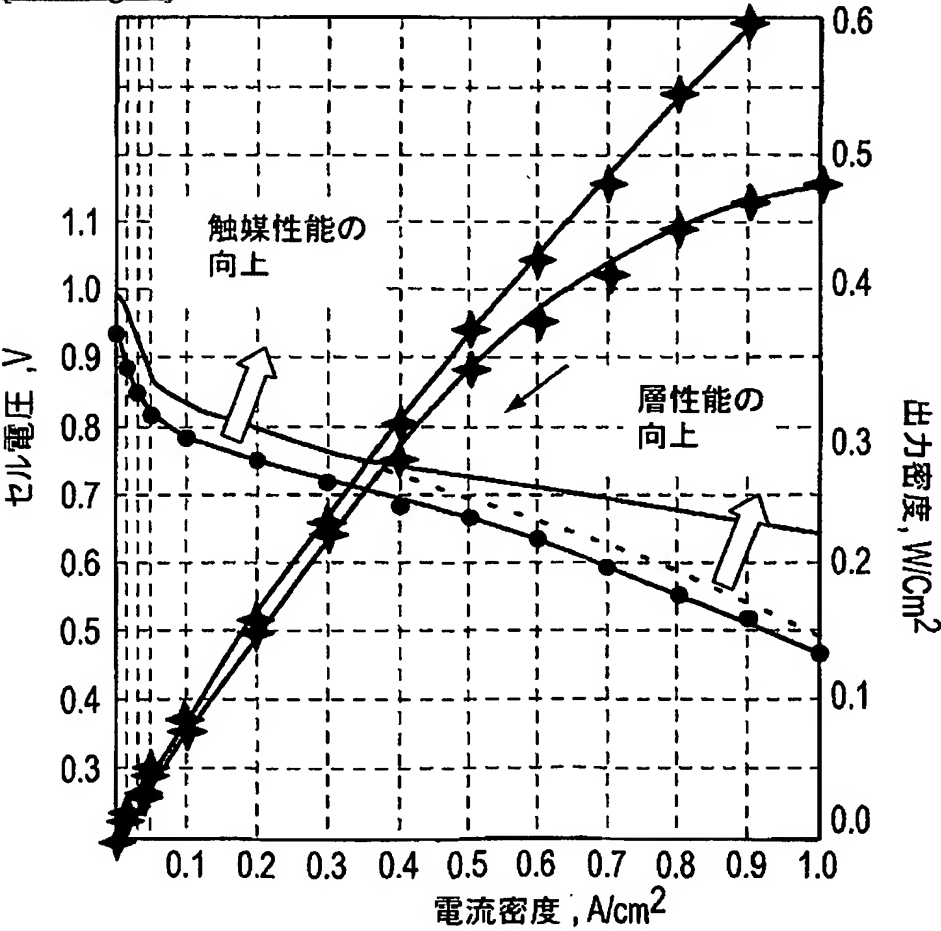
[Drawing 19]



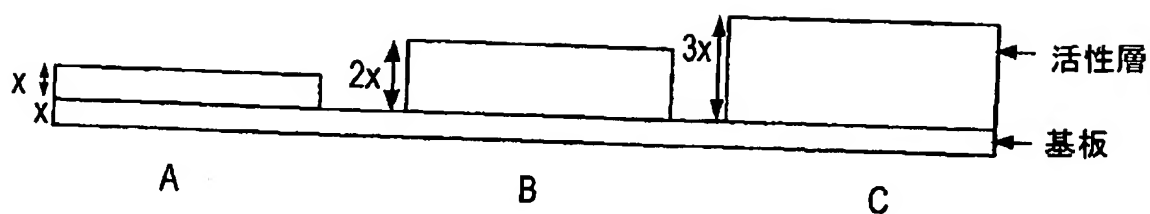
[Drawing 20]



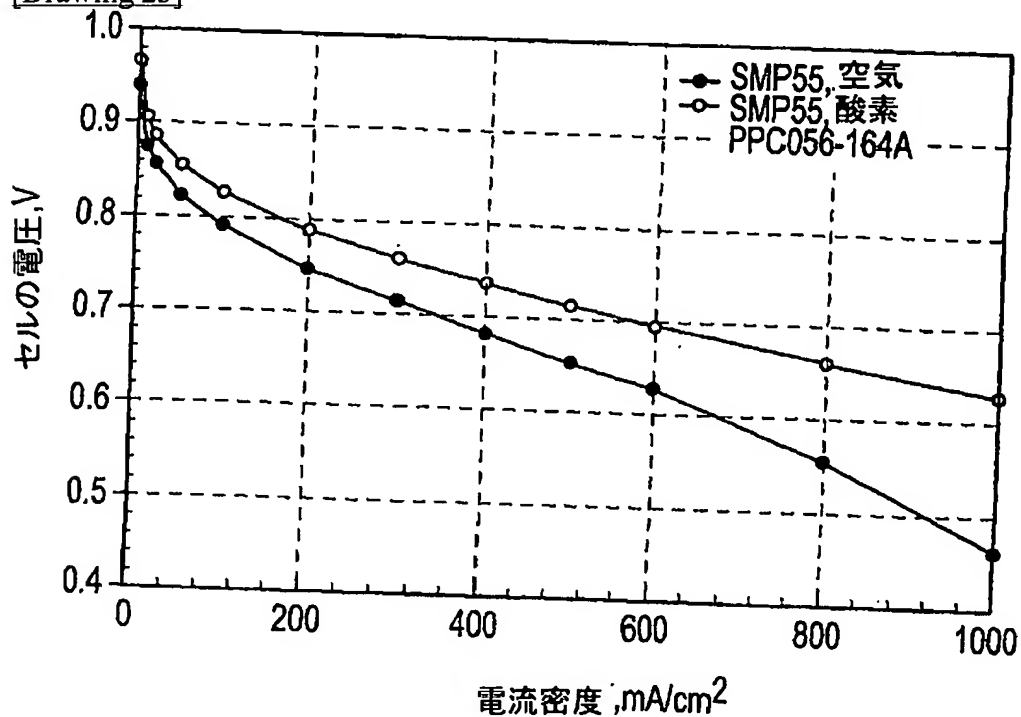
[Drawing 21]



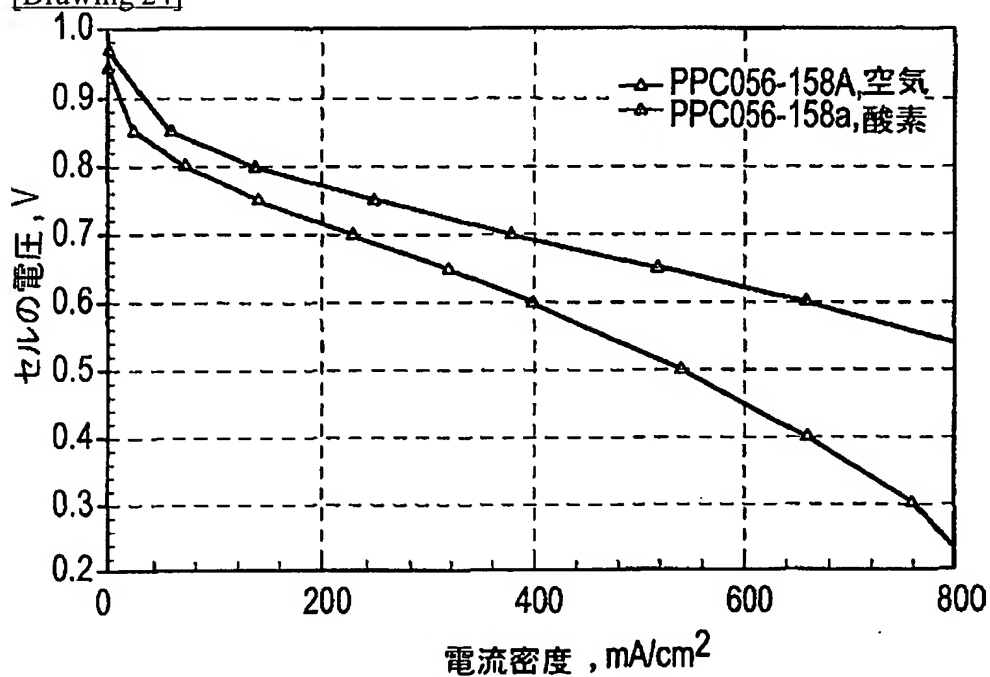
[Drawing 22]



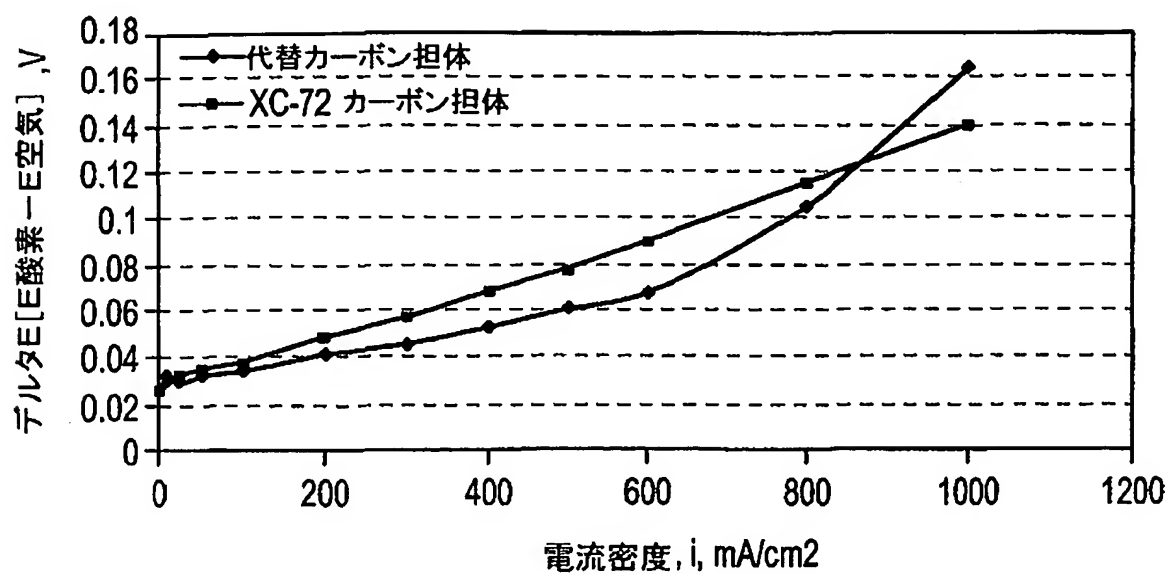
[Drawing 23]



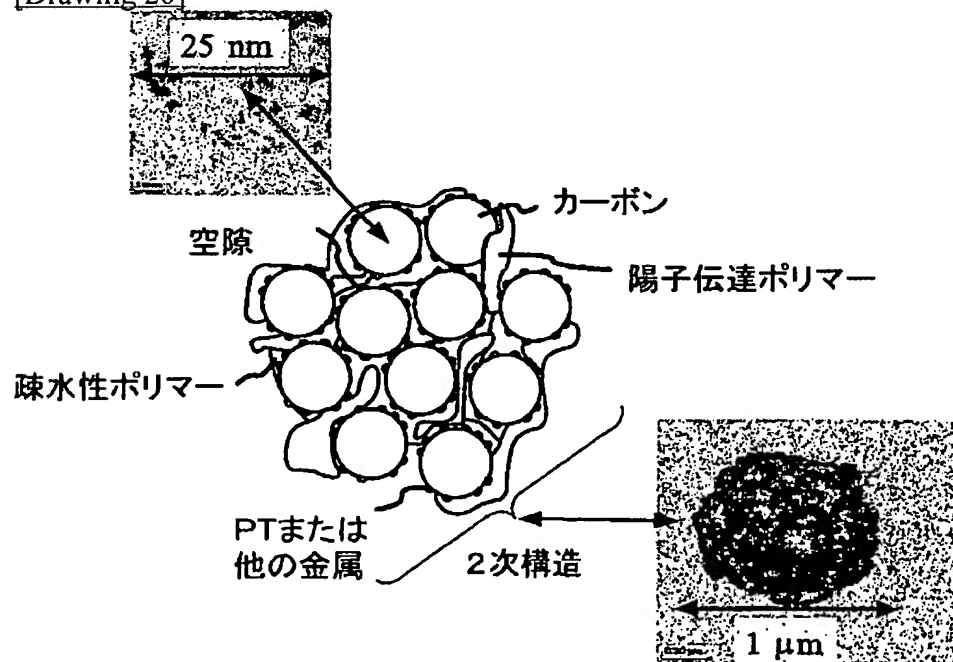
[Drawing 24]



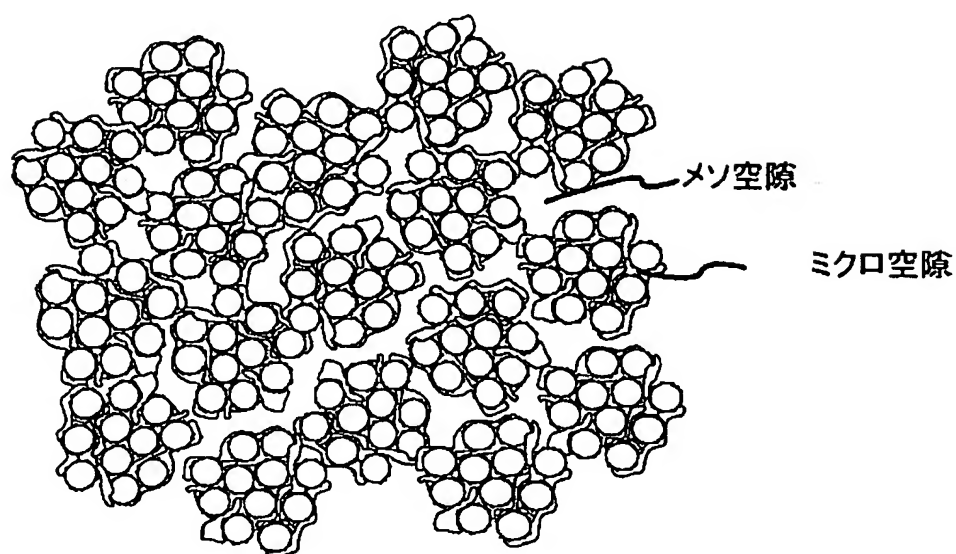
[Drawing 25]



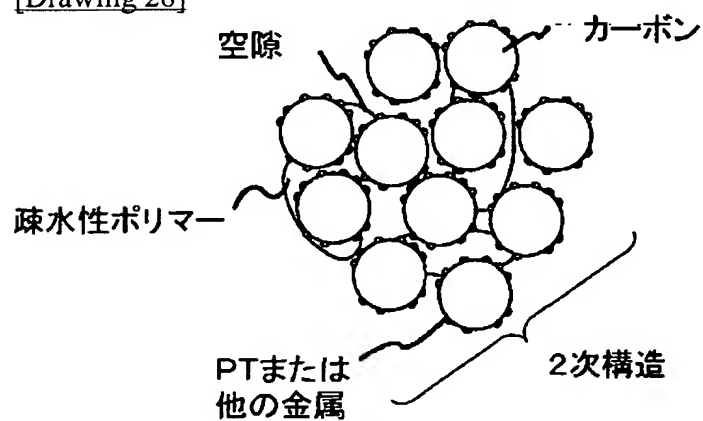
[Drawing 26]



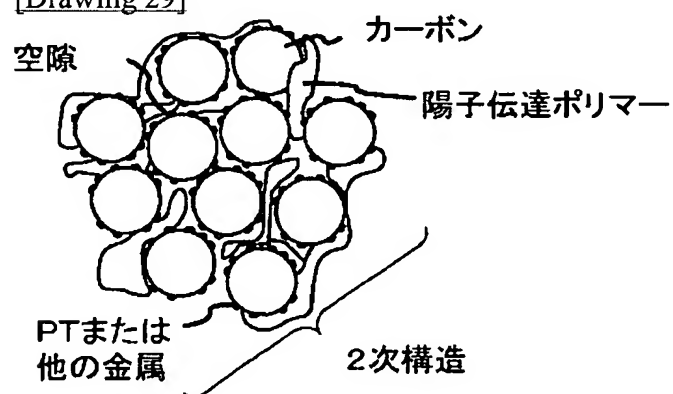
[Drawing 27]



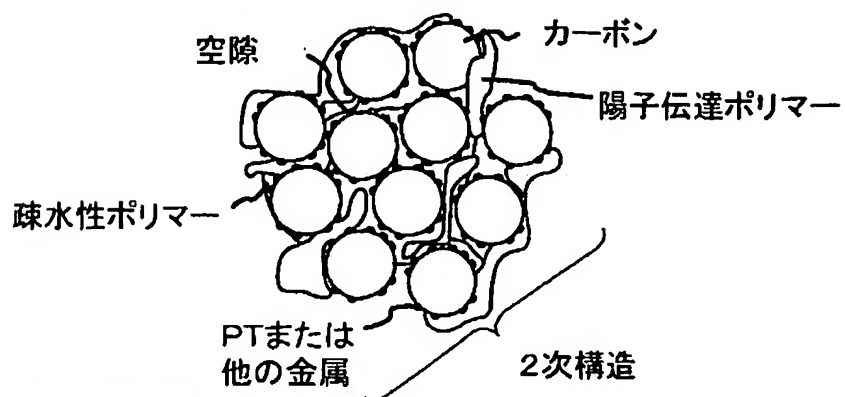
[Drawing 28]



[Drawing 29]



[Drawing 30]



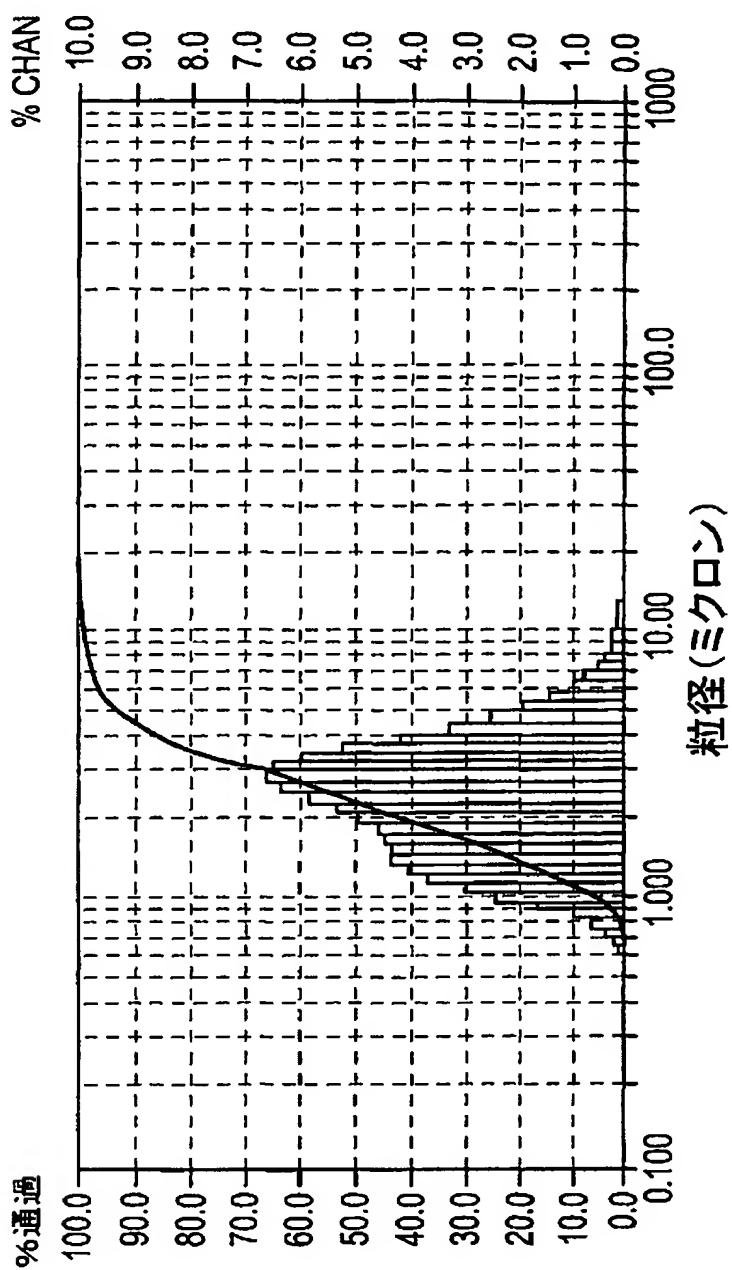
[Drawing 31]



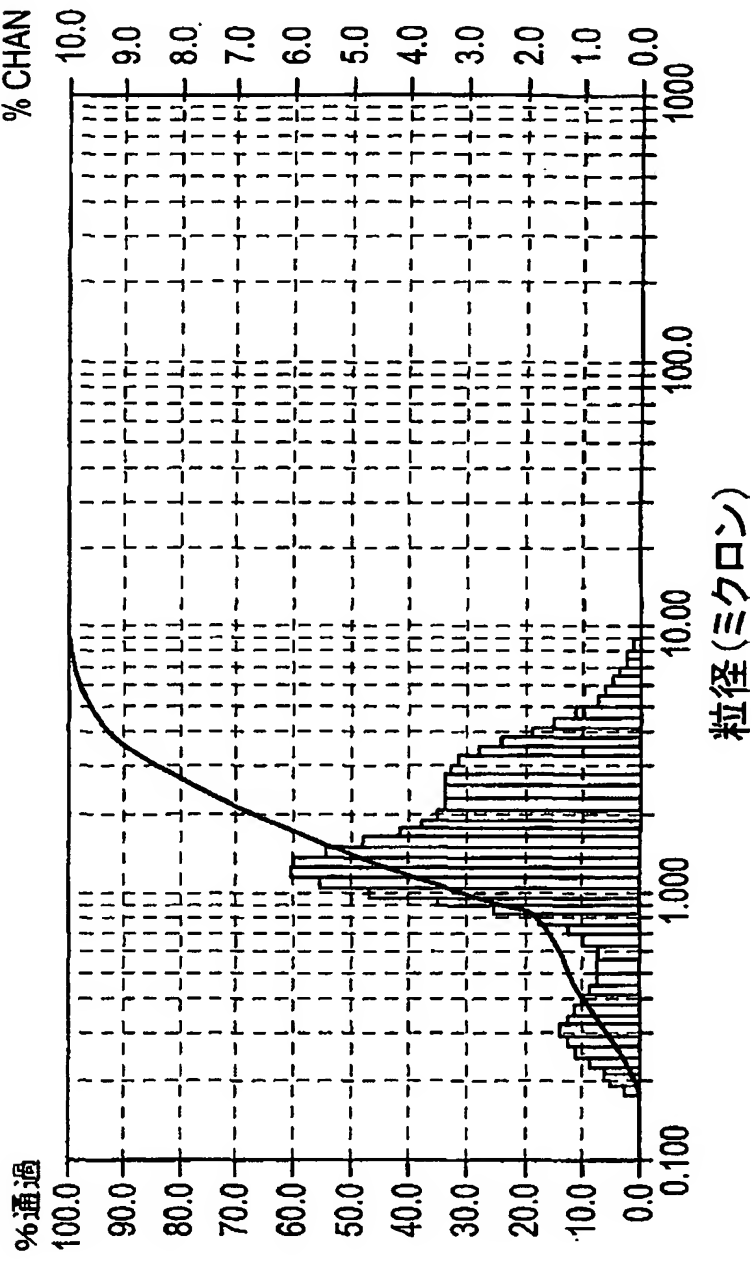
FIG.31

[Drawing 32]

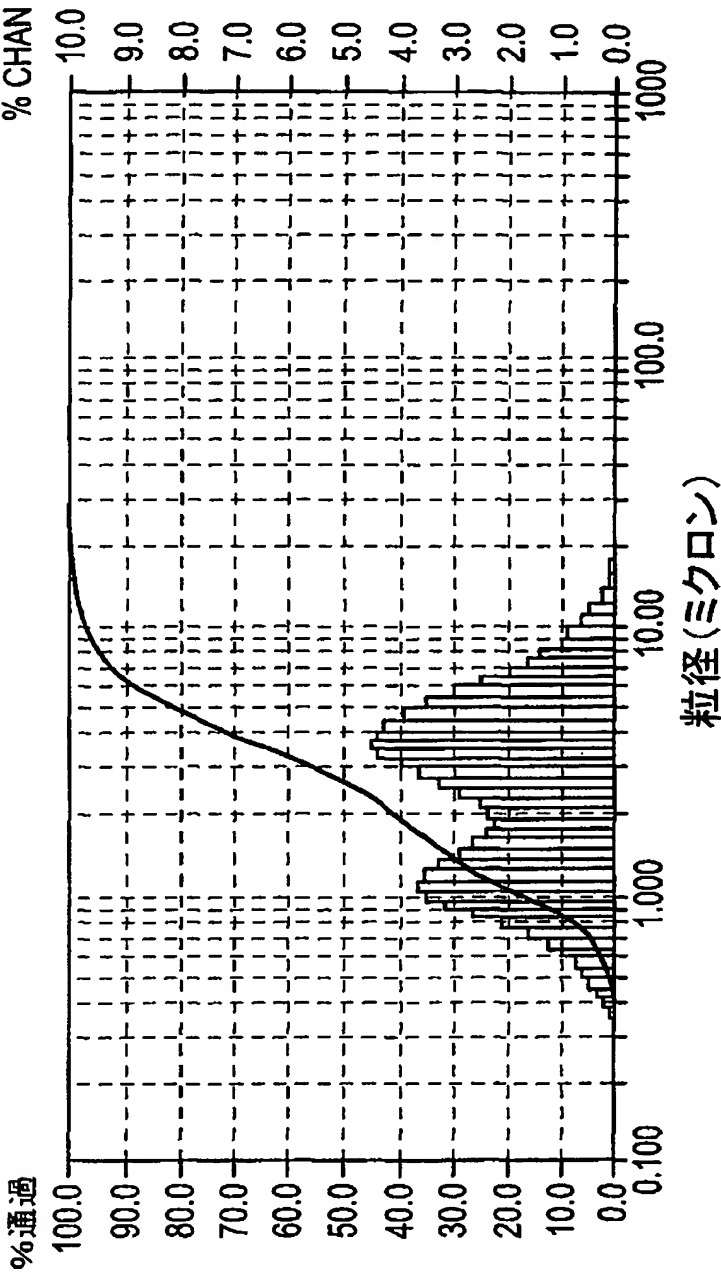


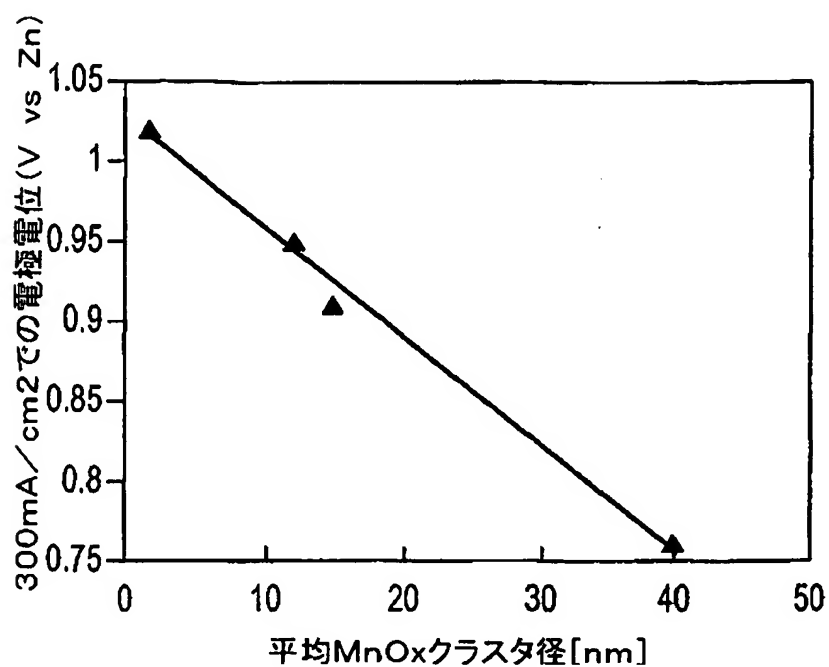


[Drawing 33]

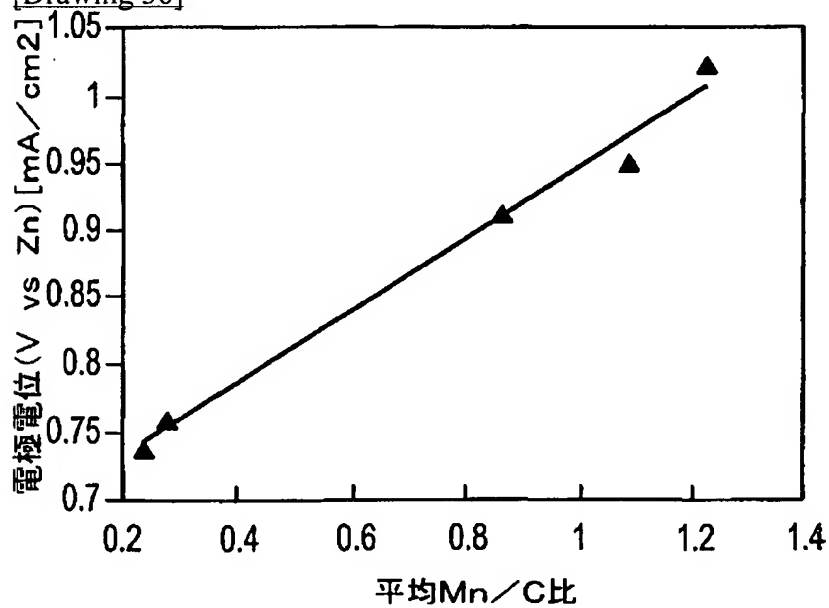


[Drawing 34]

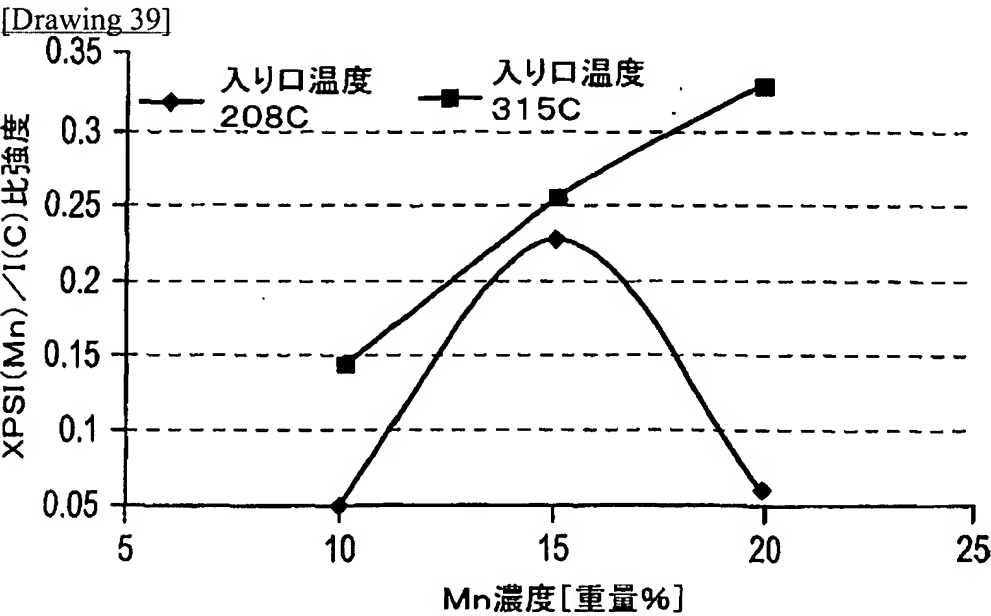
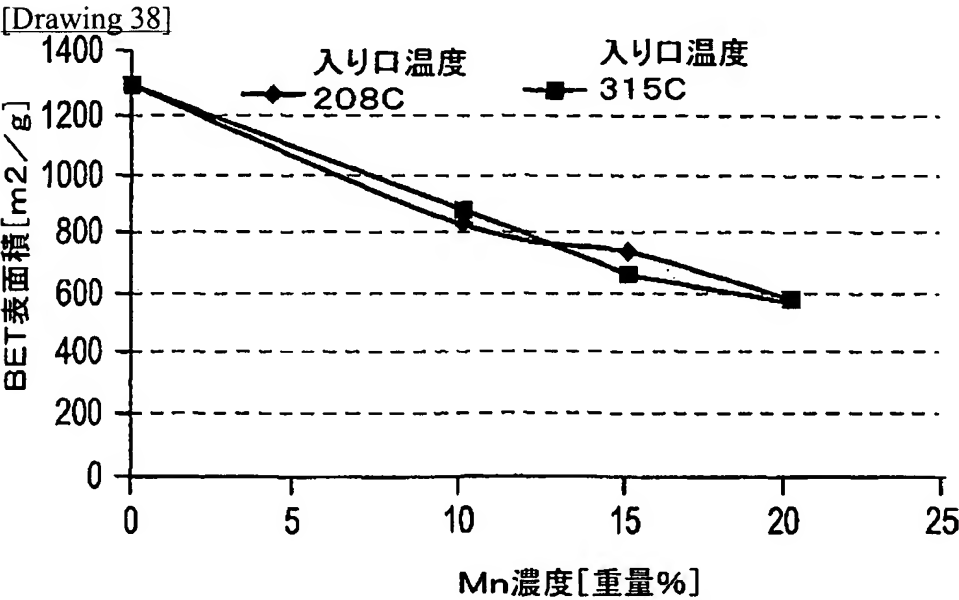
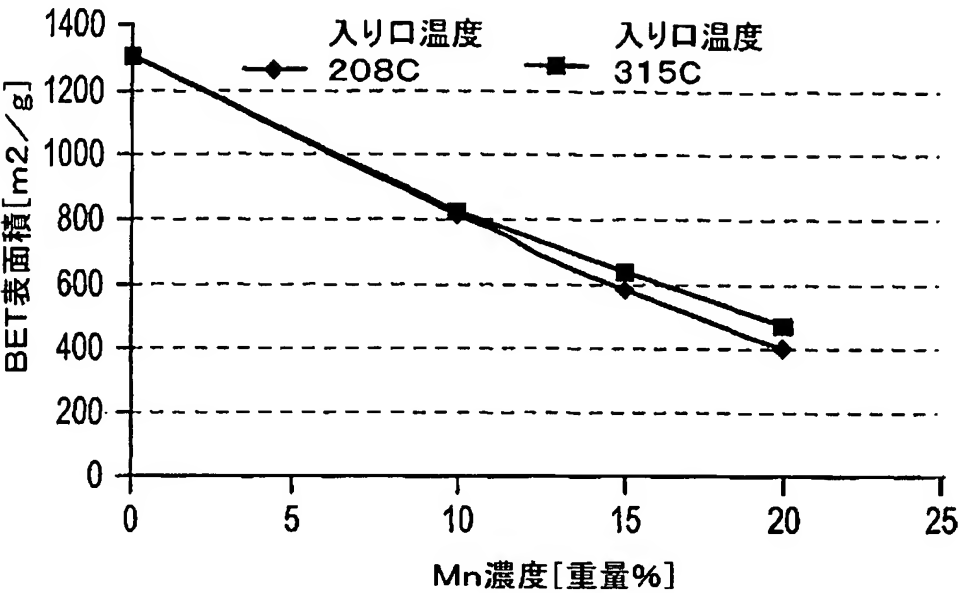




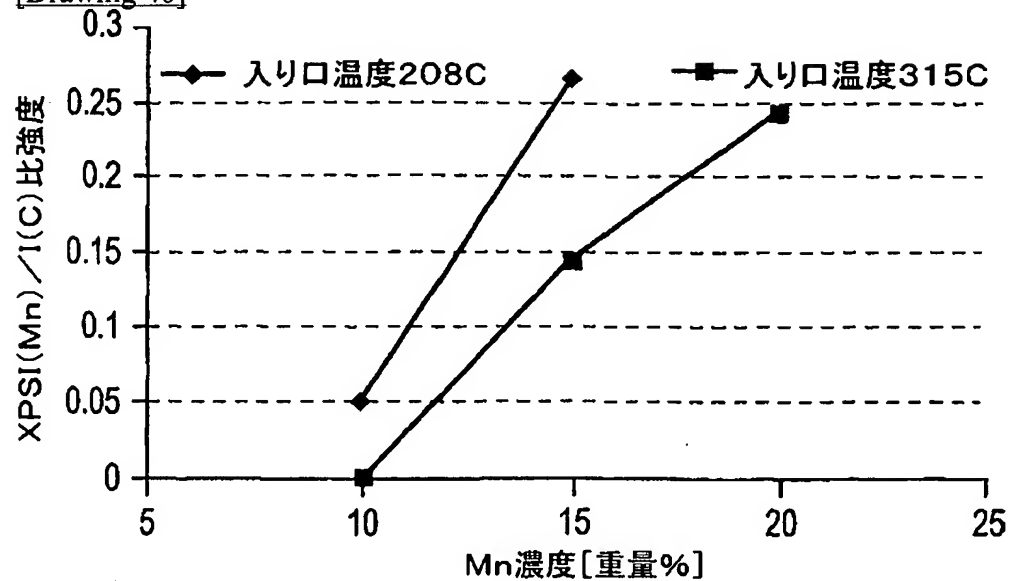
[Drawing 36]



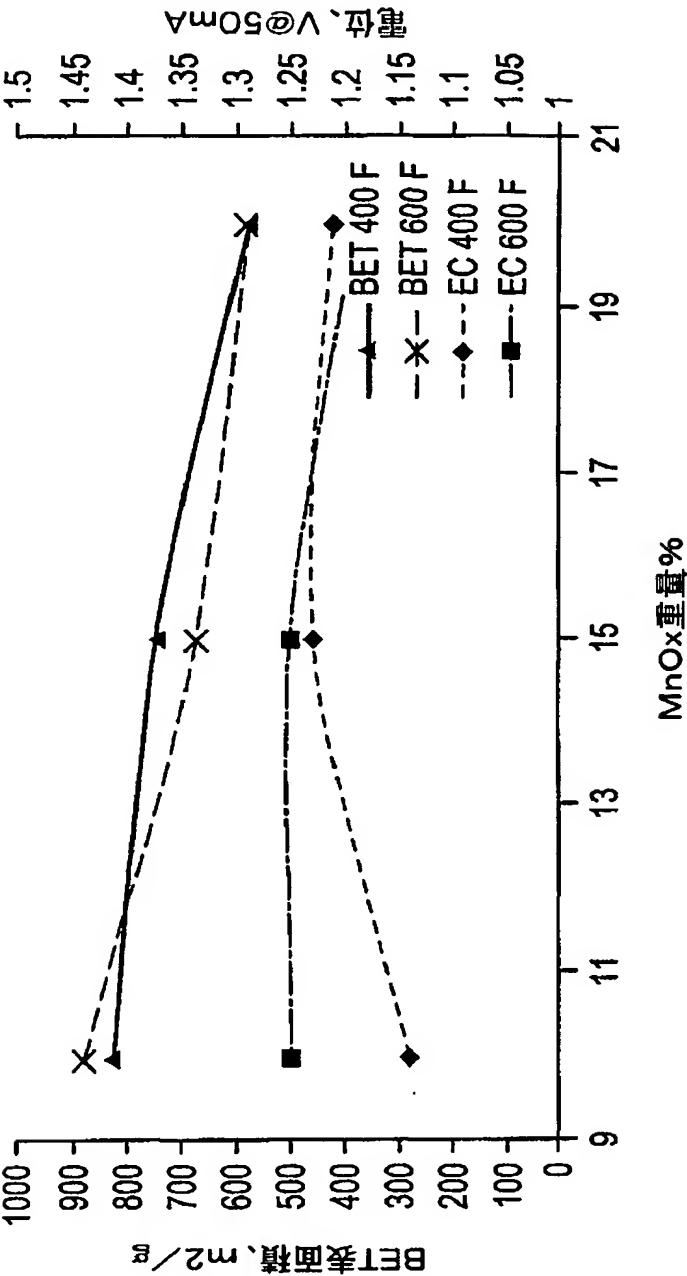
[Drawing 37]



[Drawing 40]

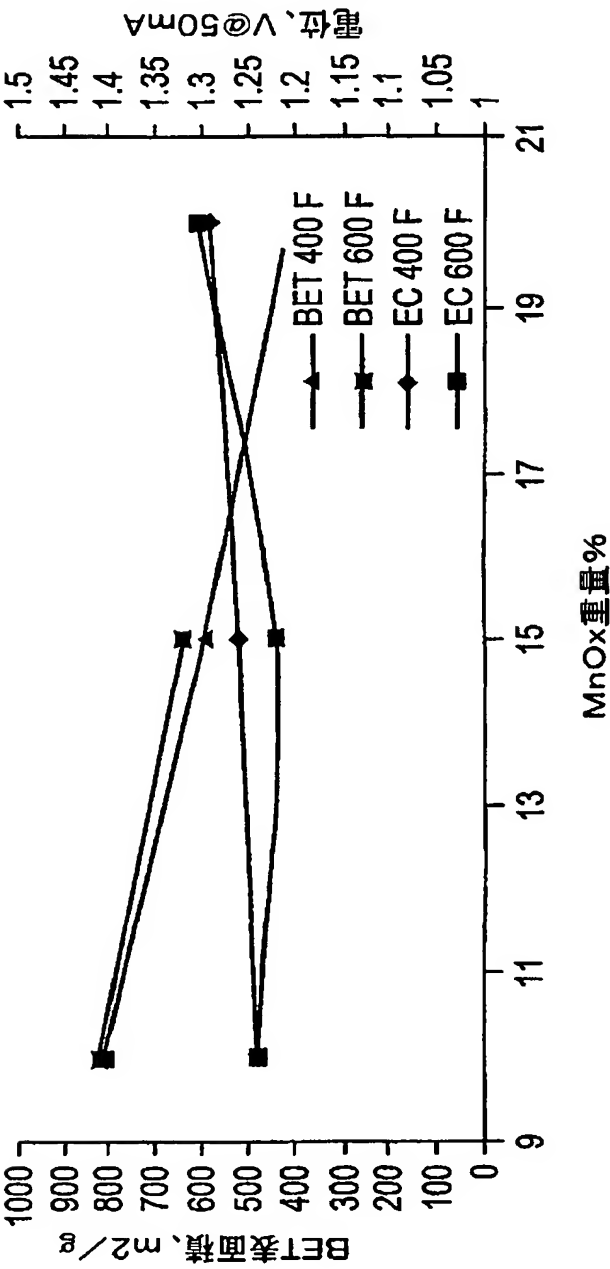


[Drawing 41]

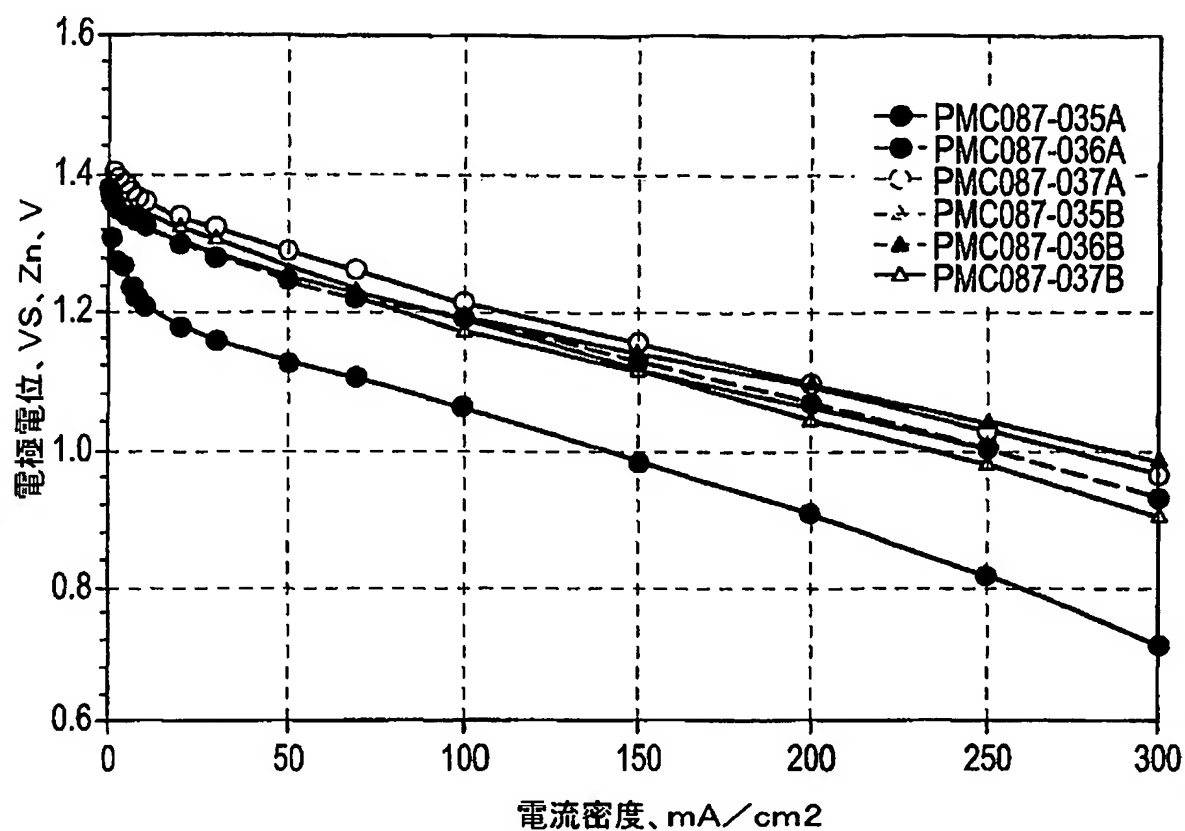


[Drawing 42]

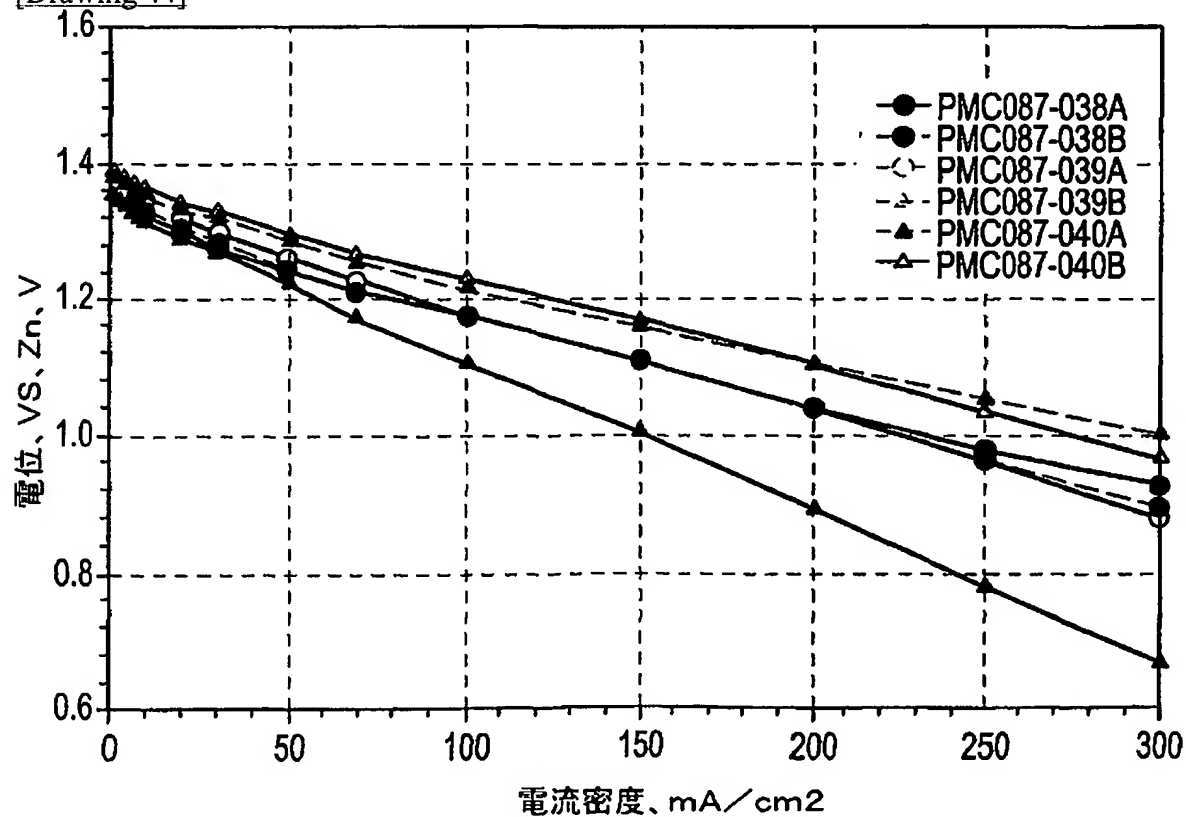




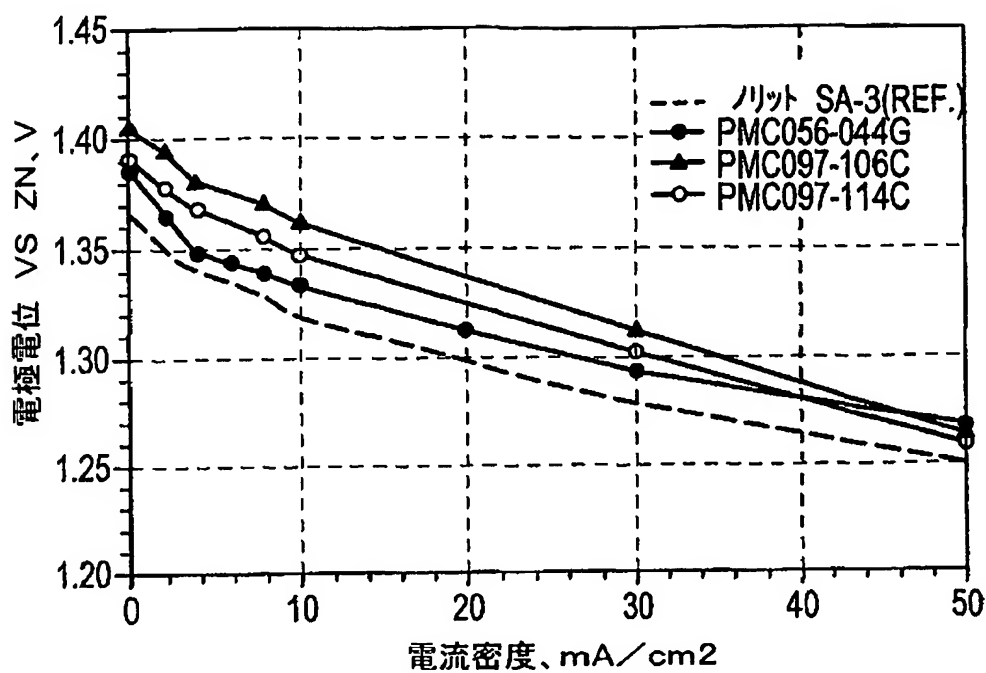
[Drawing 43]



[Drawing 44]



[Drawing 45]



[Drawing 46]

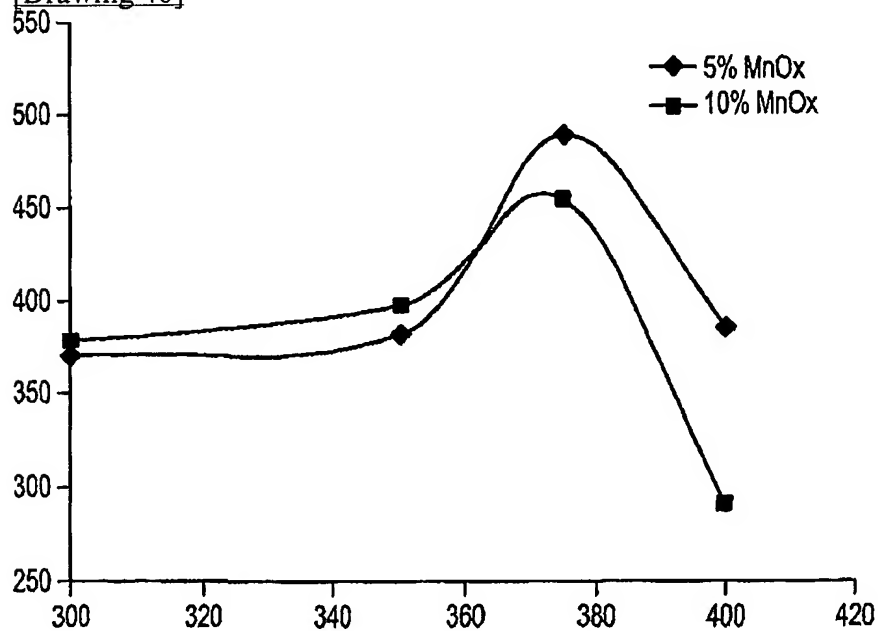
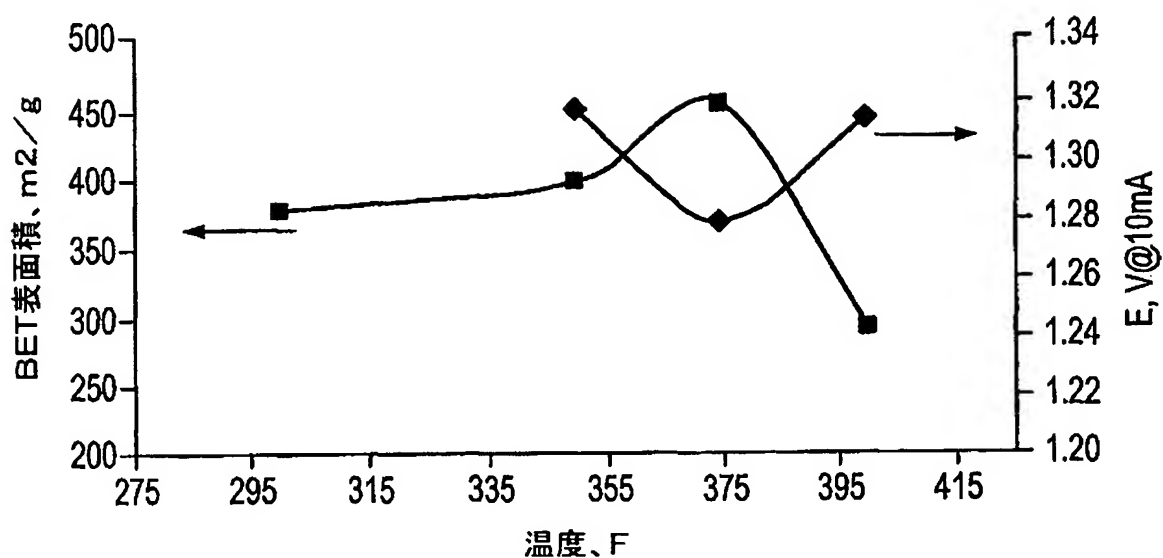
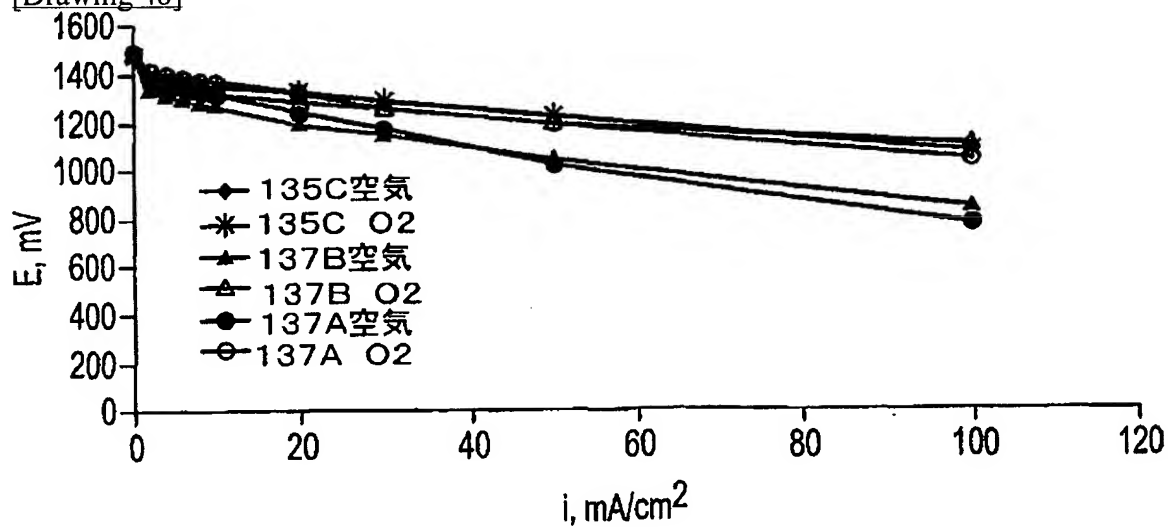


FIG.46

[Drawing 47]



[Drawing 48]



[Drawing 49]

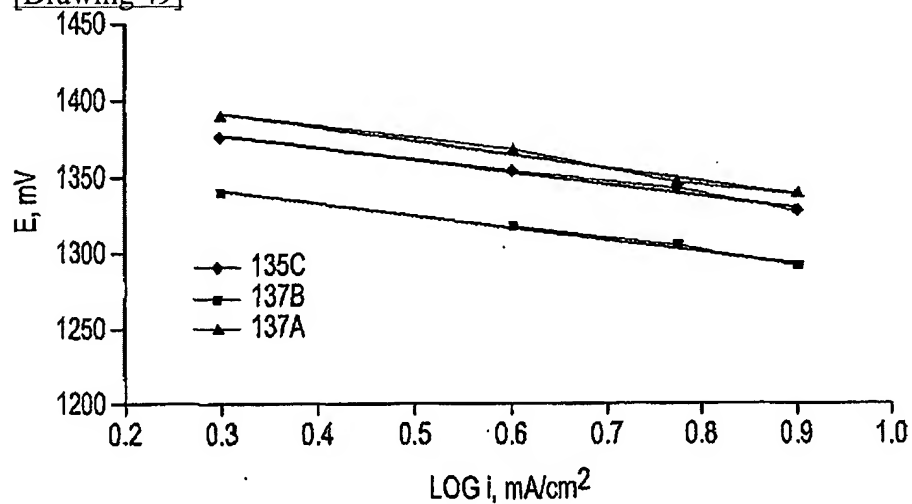


FIG.49

[Drawing 50]

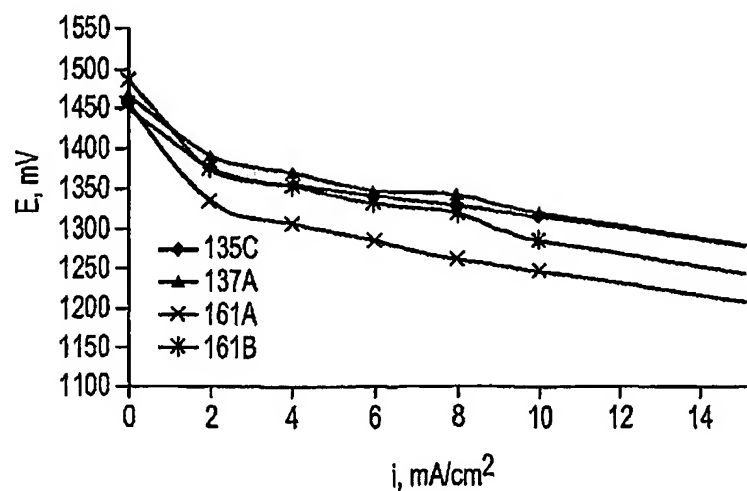


FIG.50

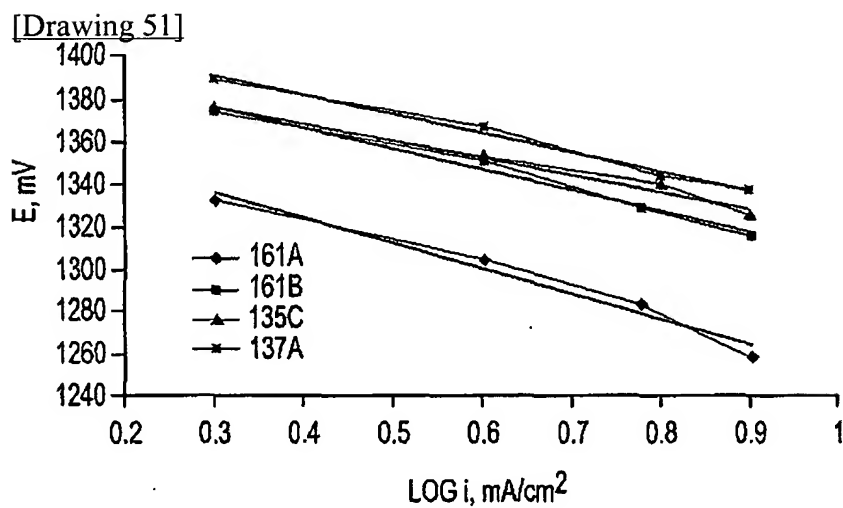


FIG.51

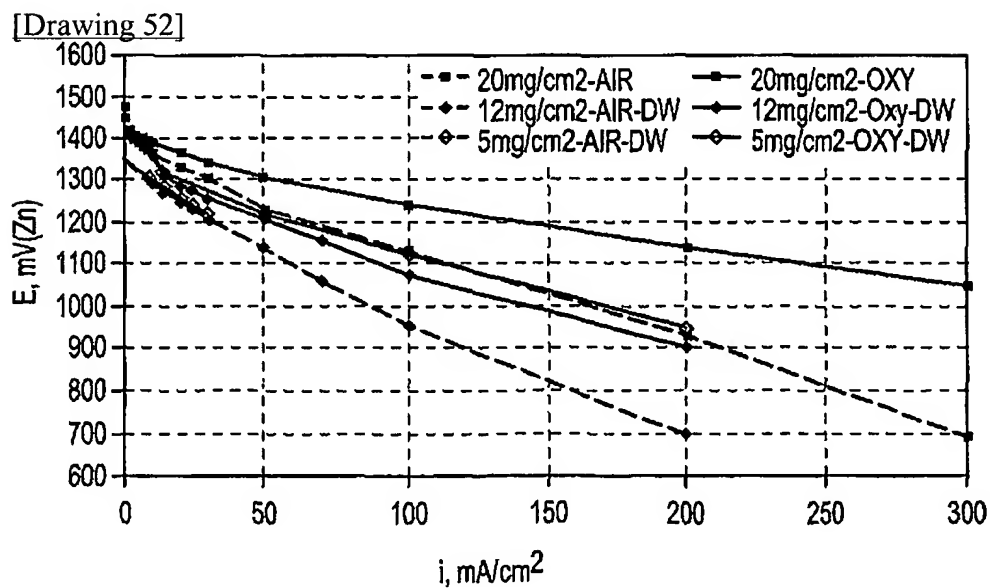
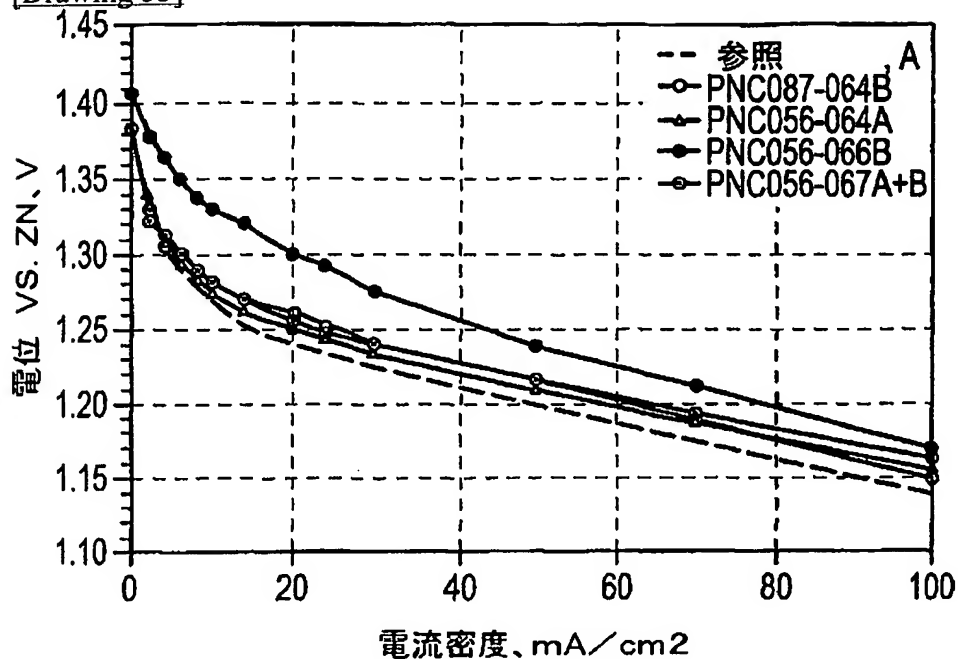
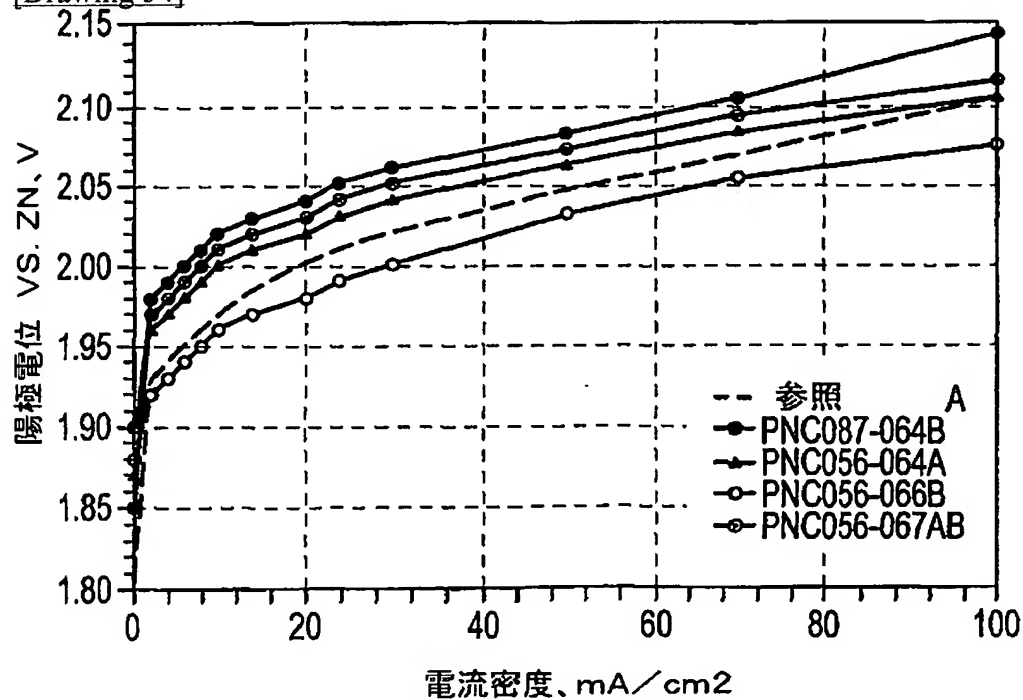


FIG.52

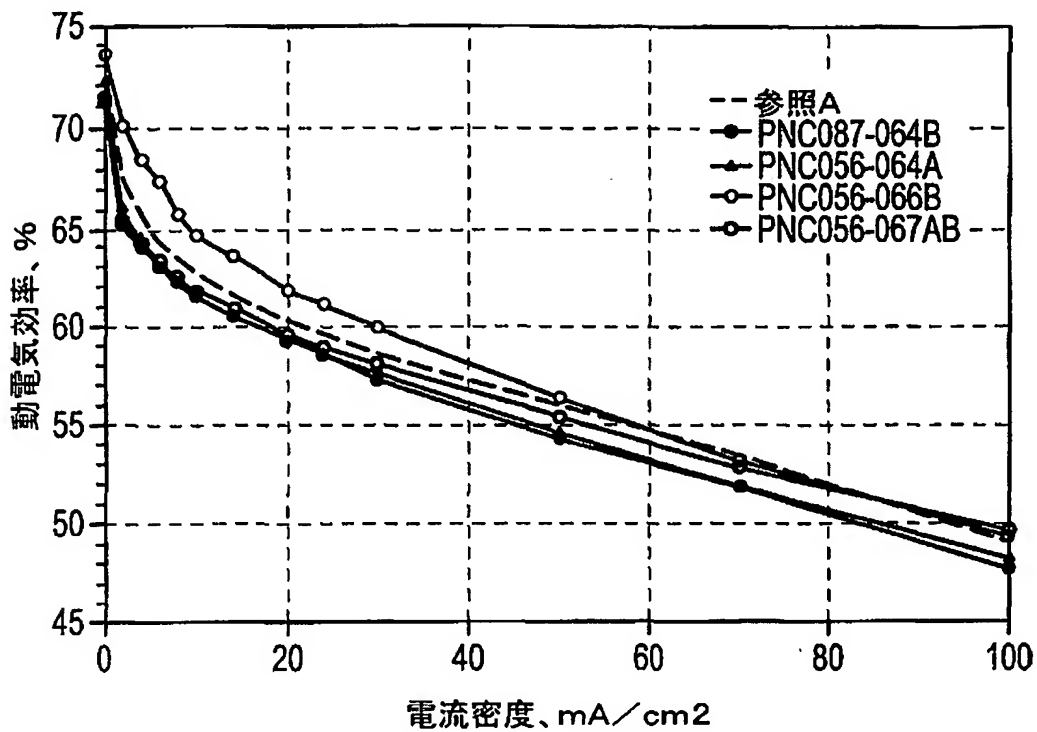
[Drawing 53]



[Drawing 54]



[Drawing 55]



[Drawing 56]

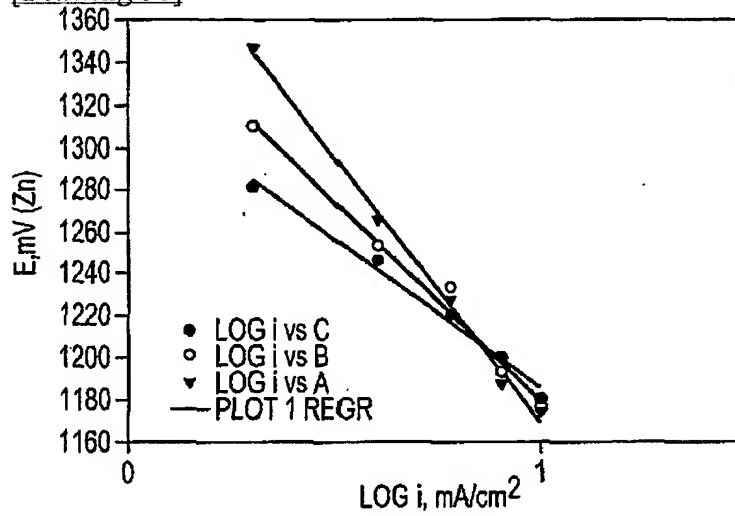


FIG.56

[Drawing 57]

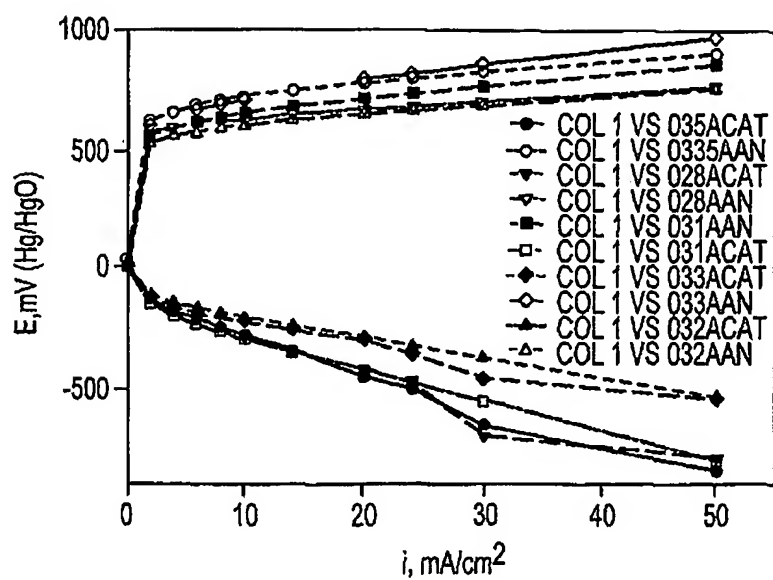


FIG.57

[Drawing 58]

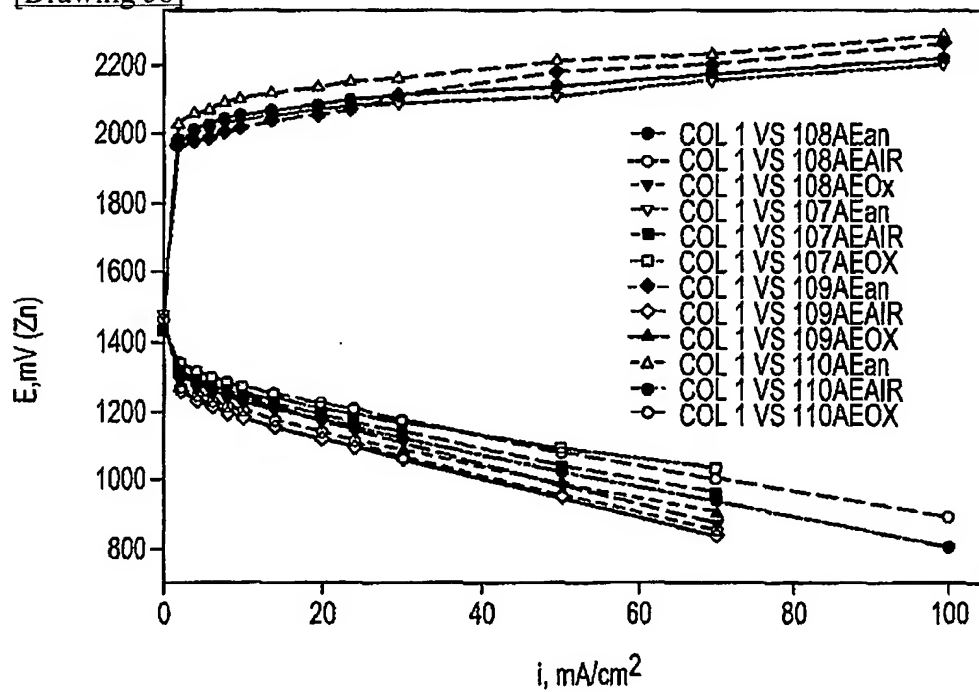


FIG.58

[Drawing 59]



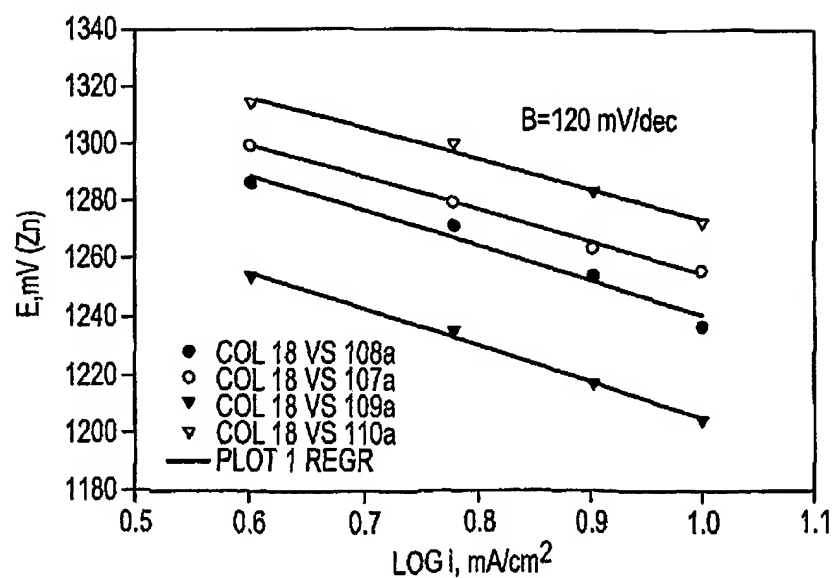
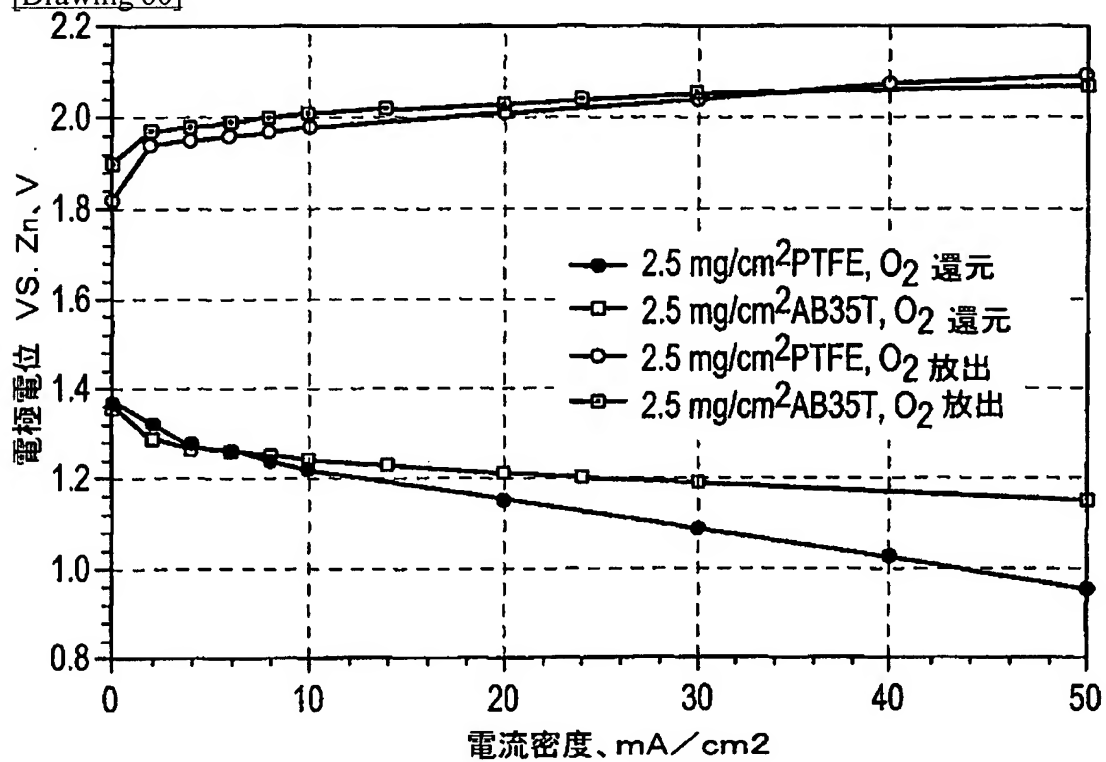
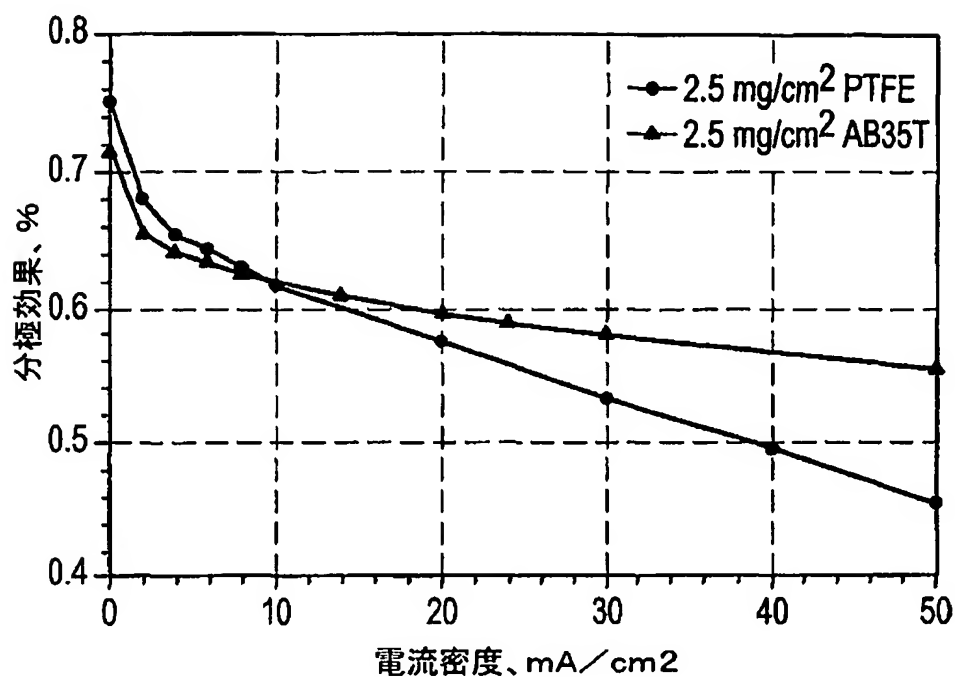


FIG.59

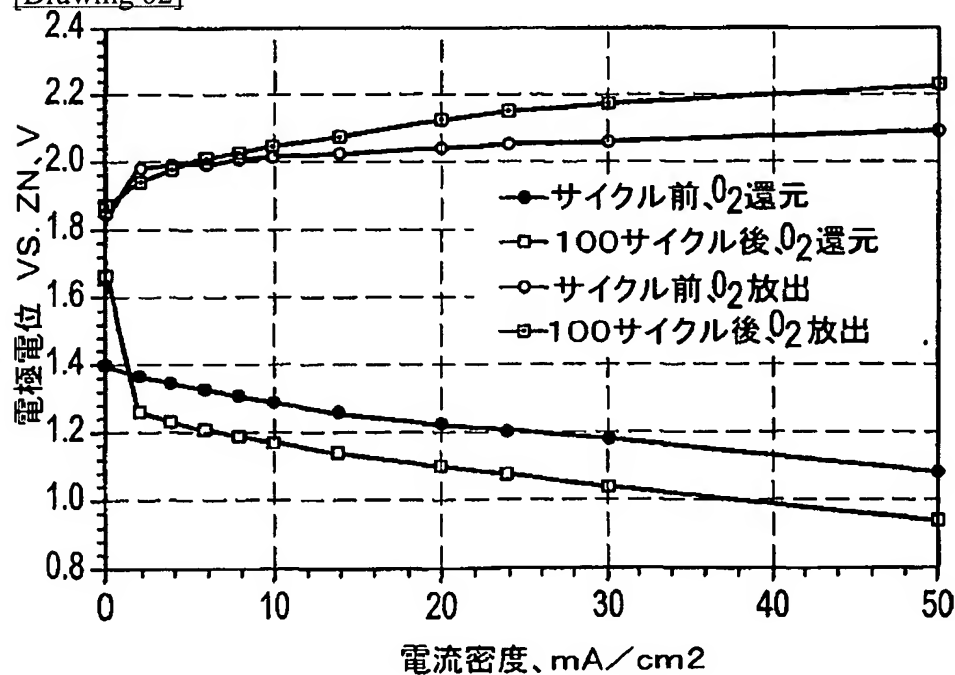
[Drawing 60]



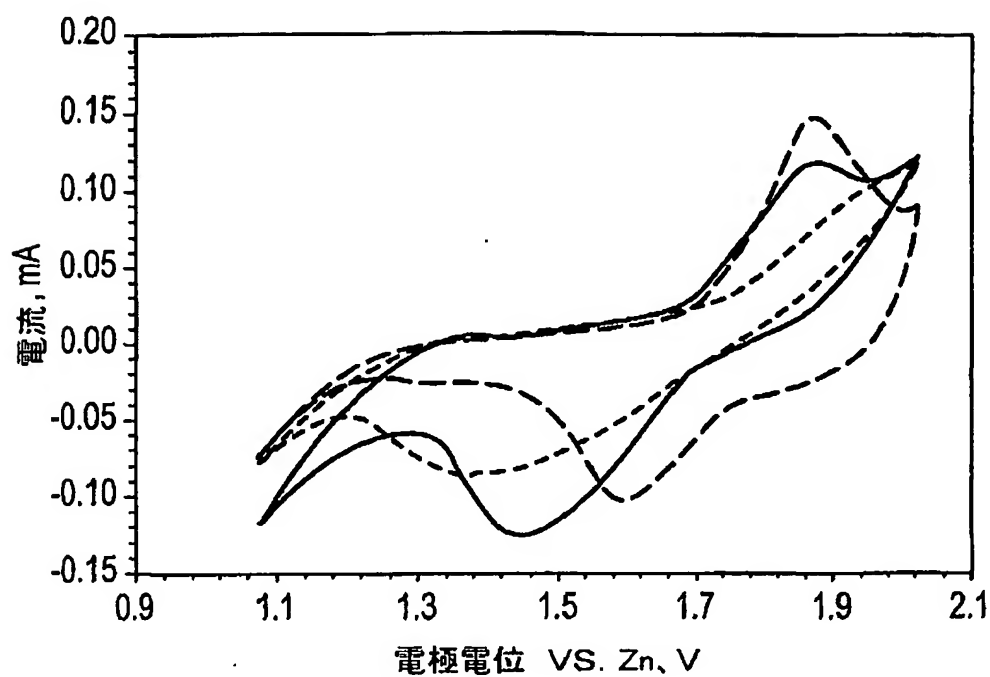
[Drawing 61]



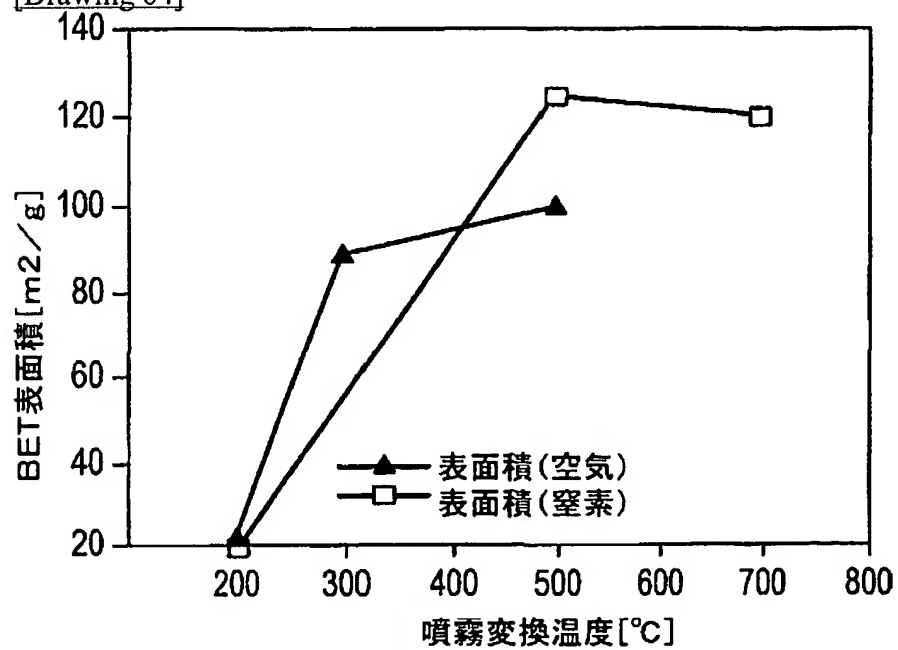
[Drawing 62]



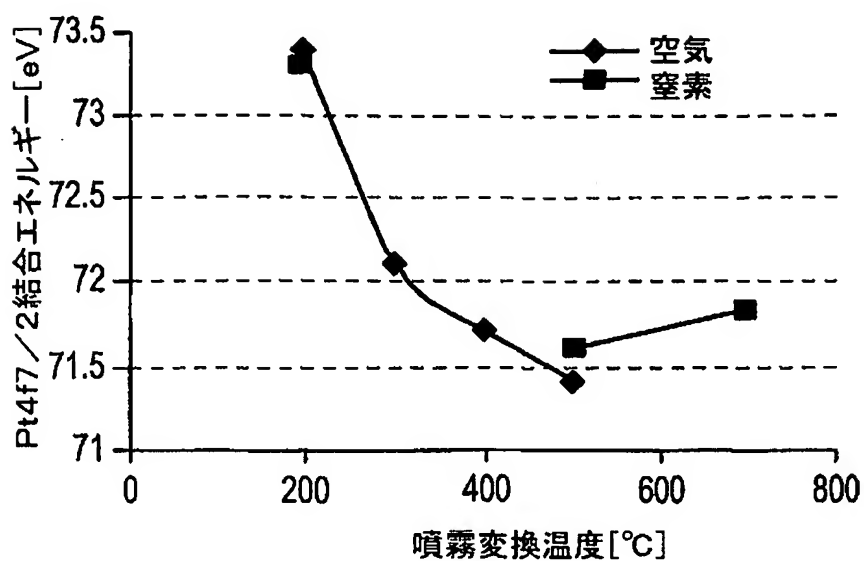
[Drawing 63]



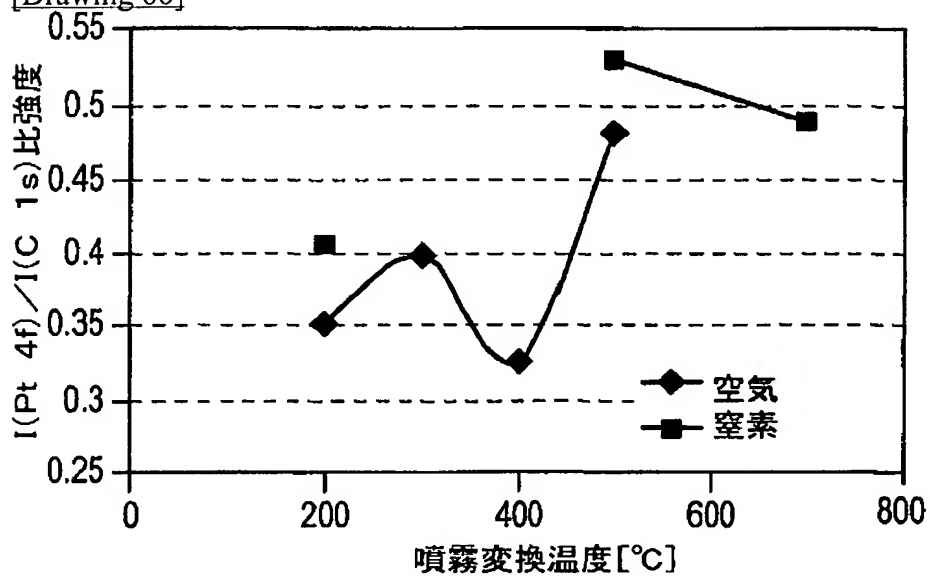
[Drawing 64]



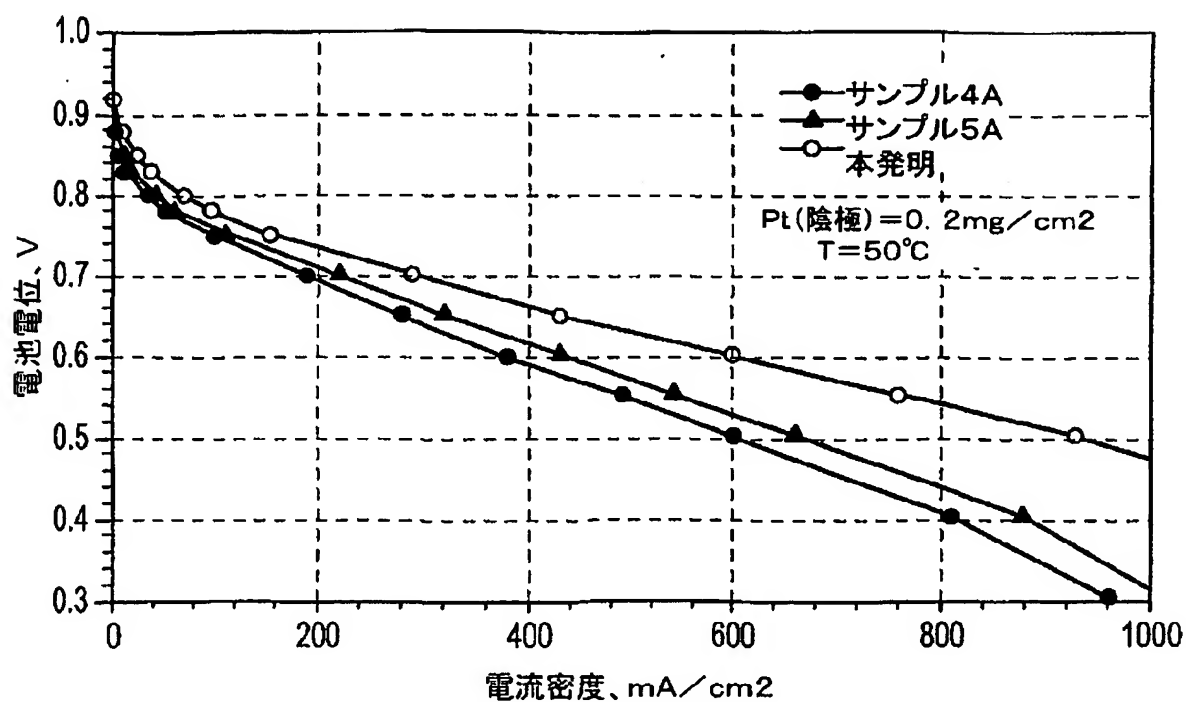
[Drawing 65]



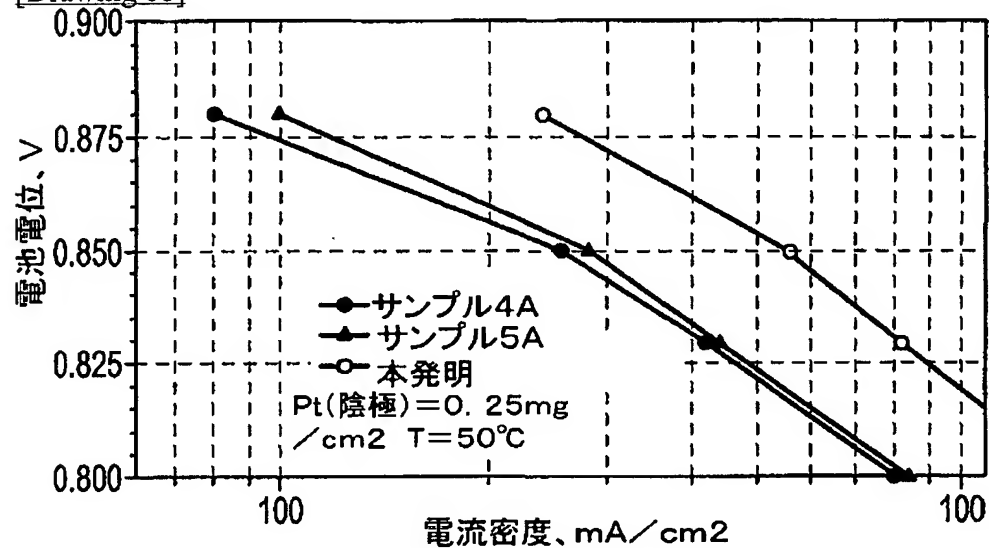
[Drawing 66]



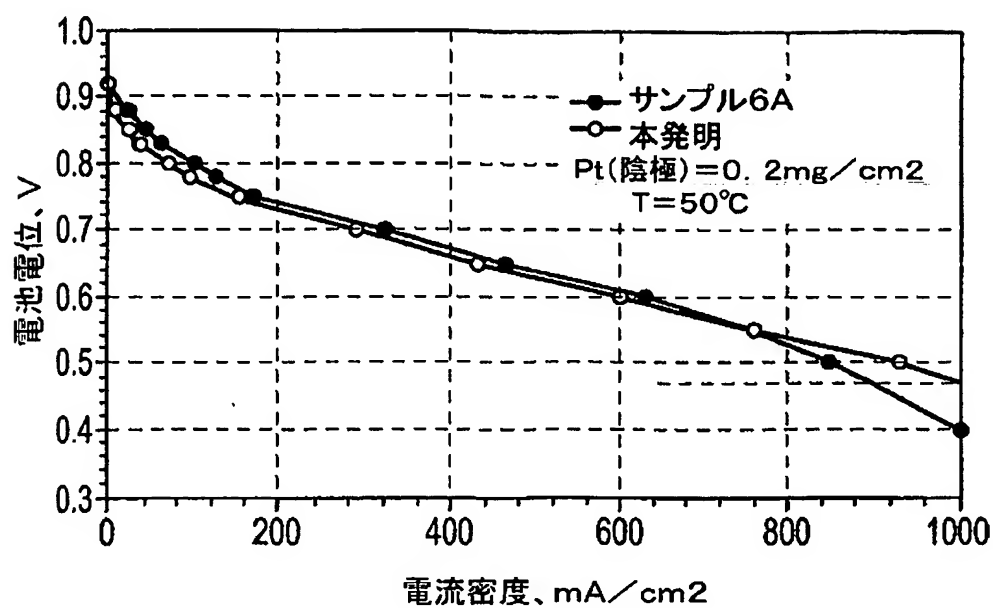
[Drawing 67]



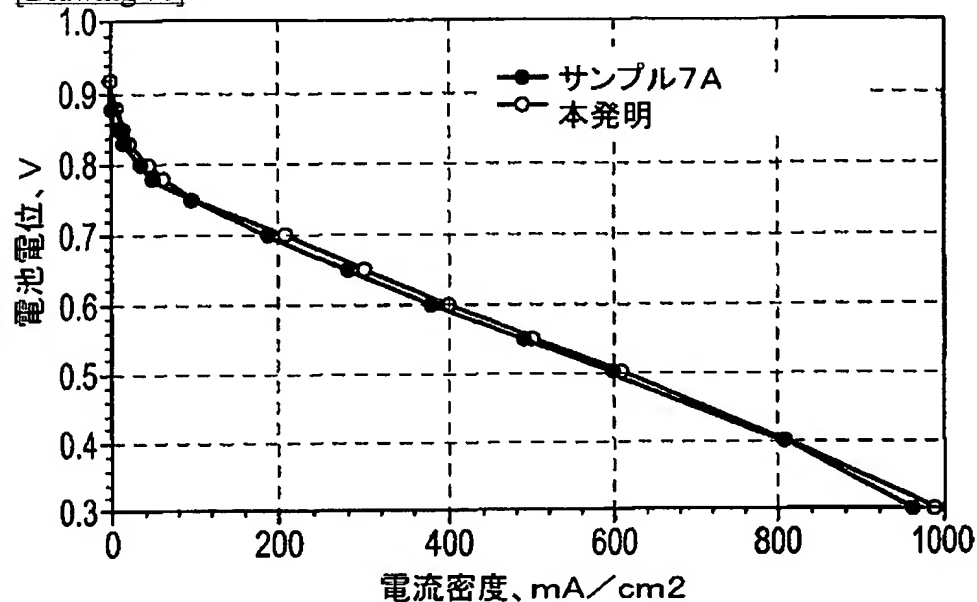
[Drawing 68]



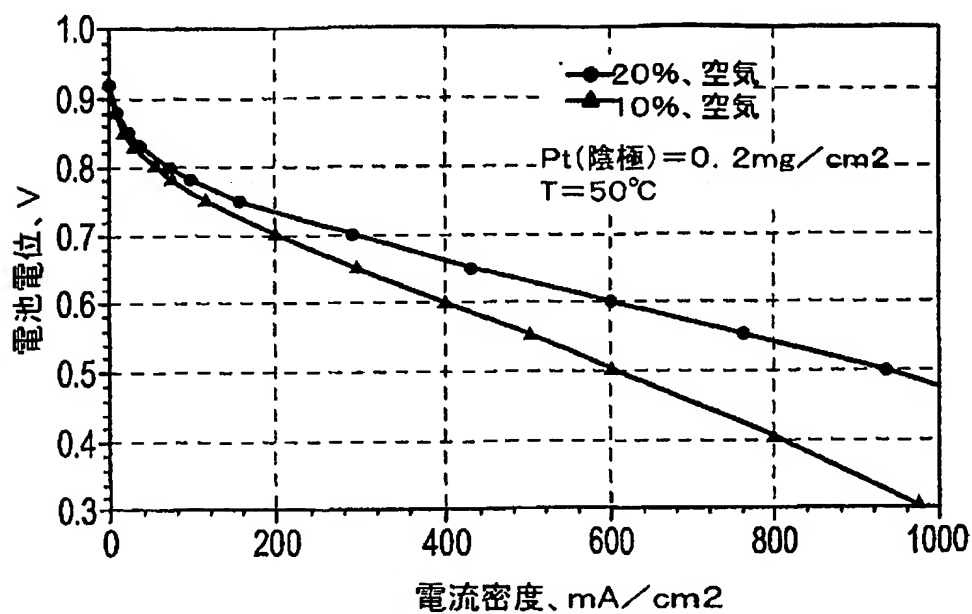
[Drawing 69]



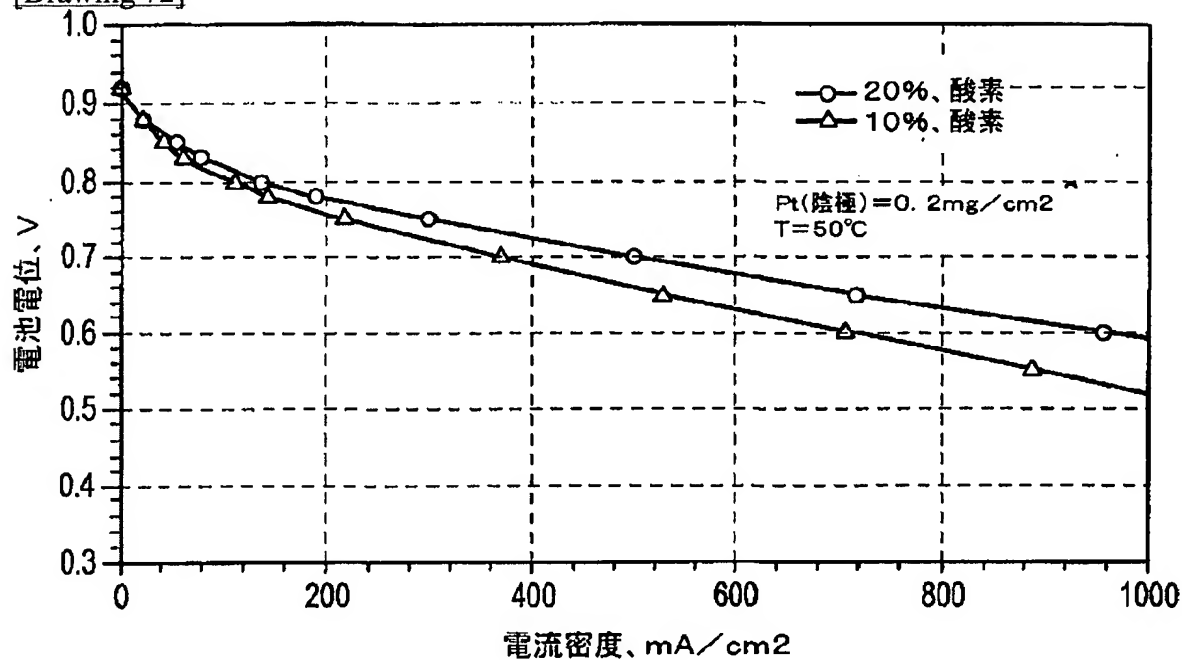
[Drawing 70]



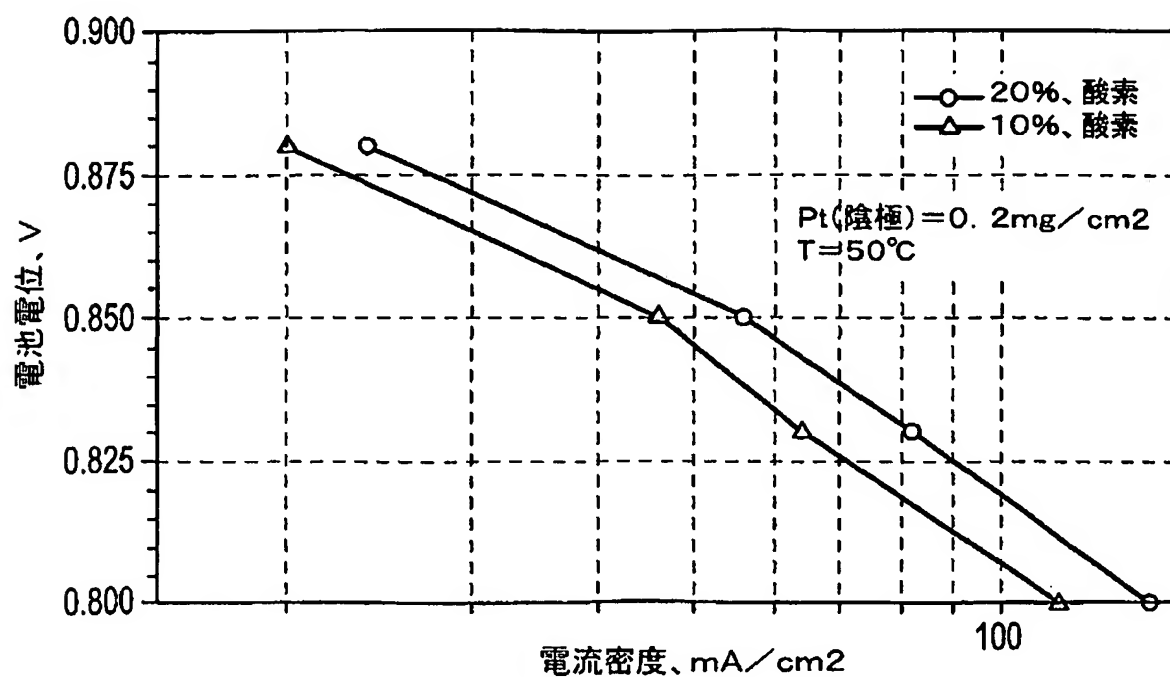
[Drawing 71]



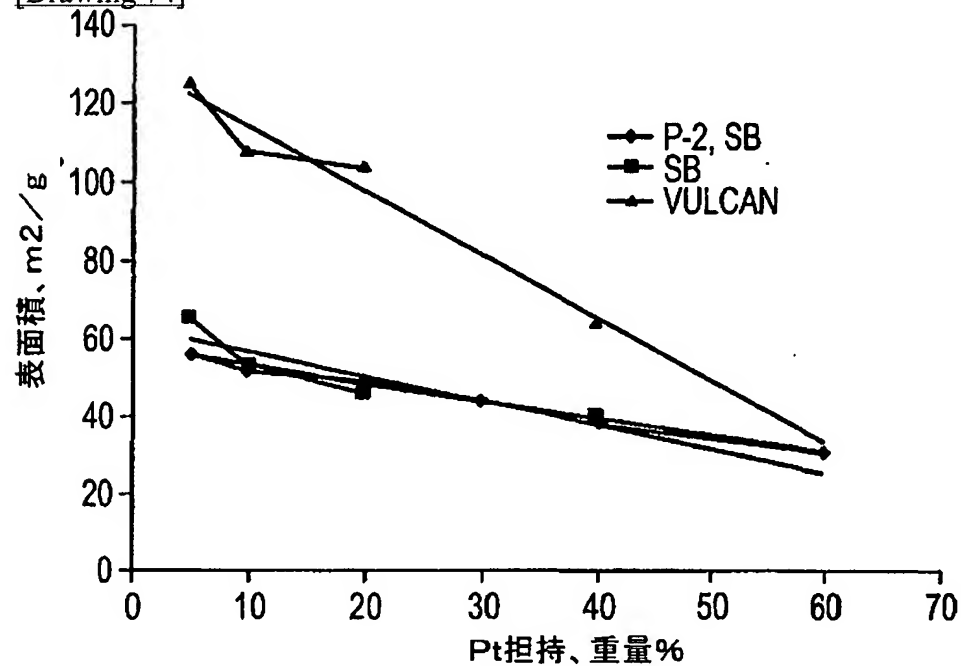
[Drawing 72]



[Drawing 73]

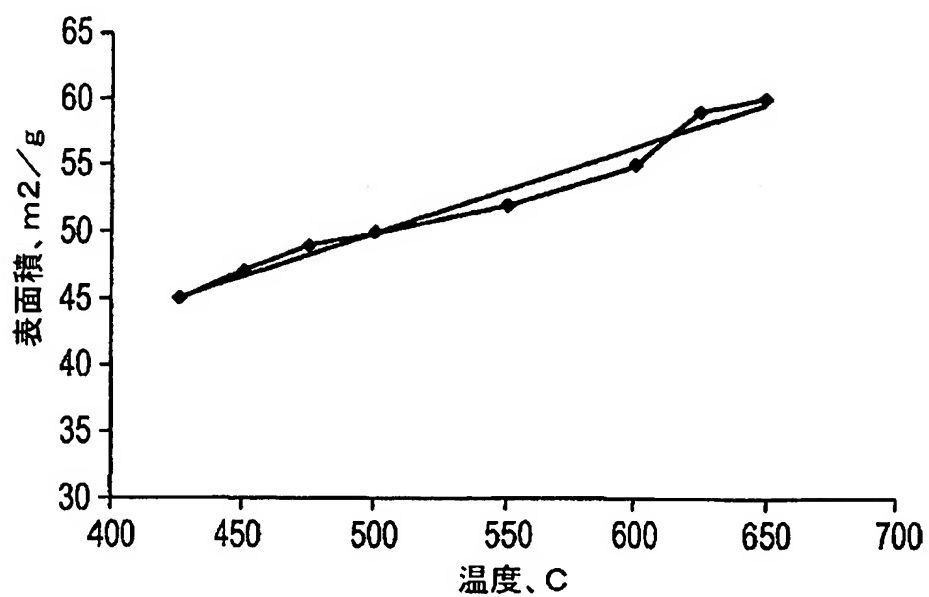


[Drawing 74]

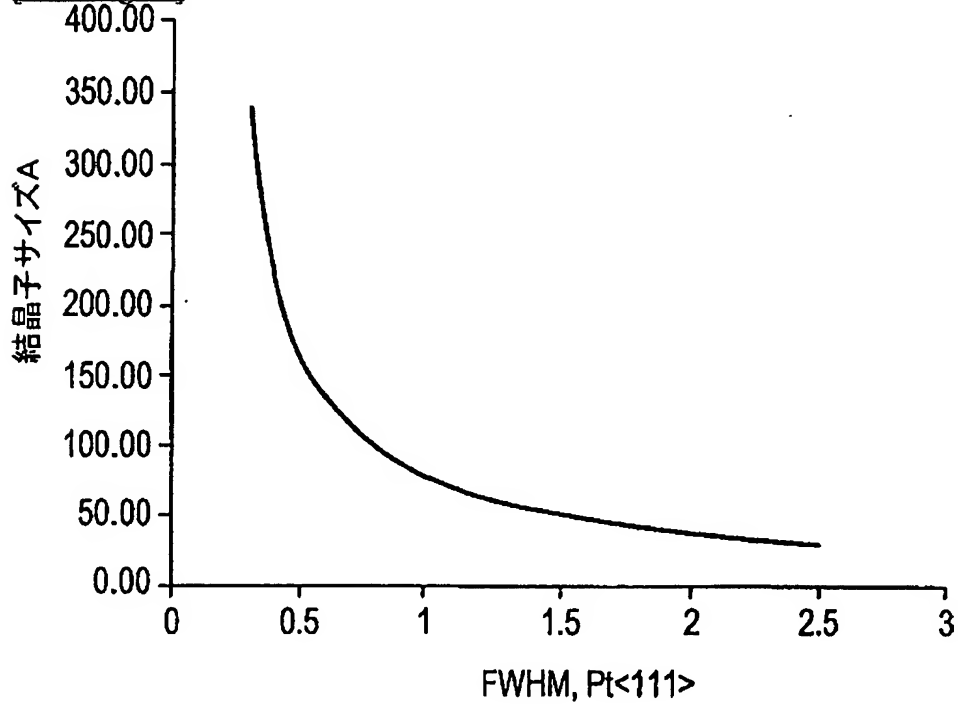


[Drawing 75]

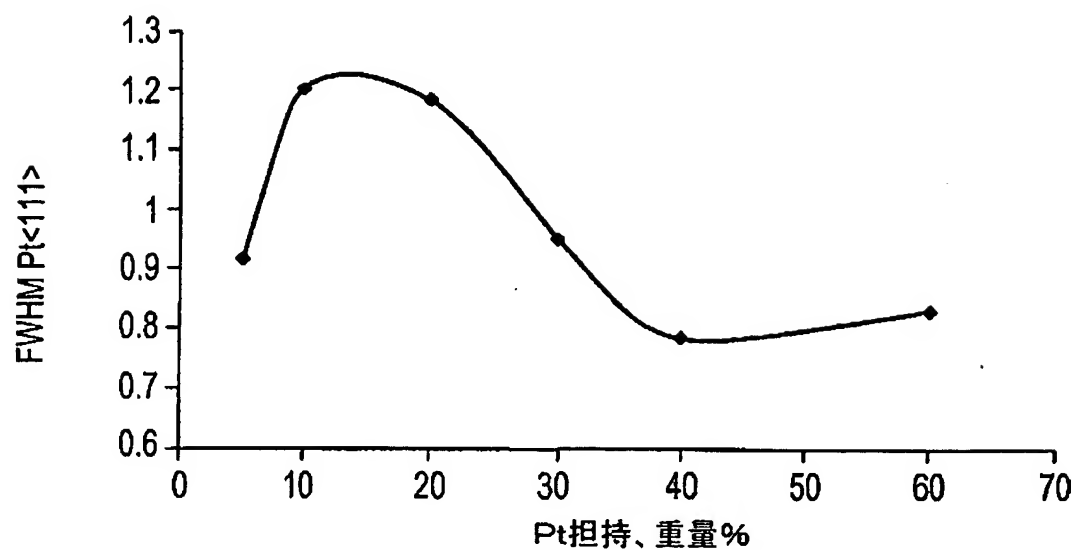




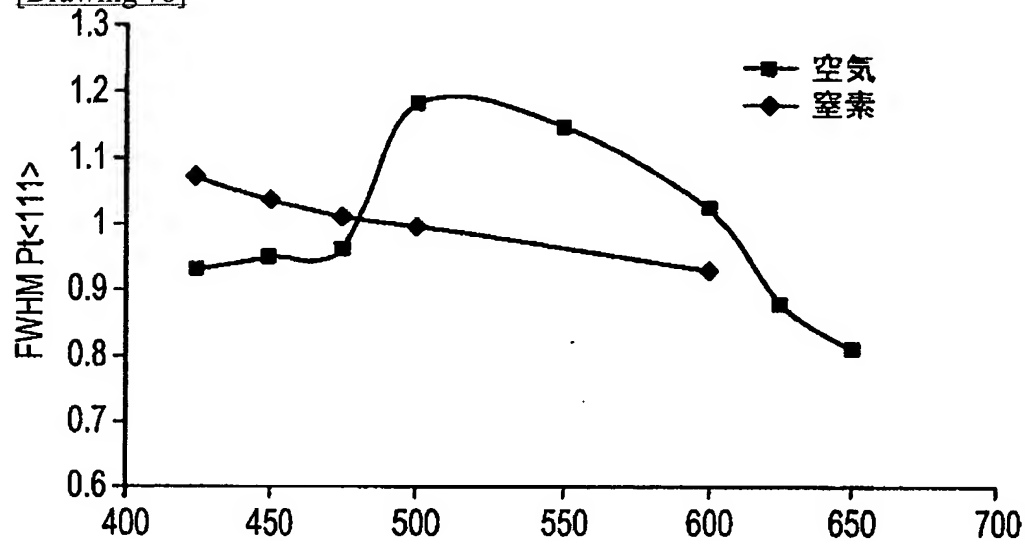
[Drawing 76]



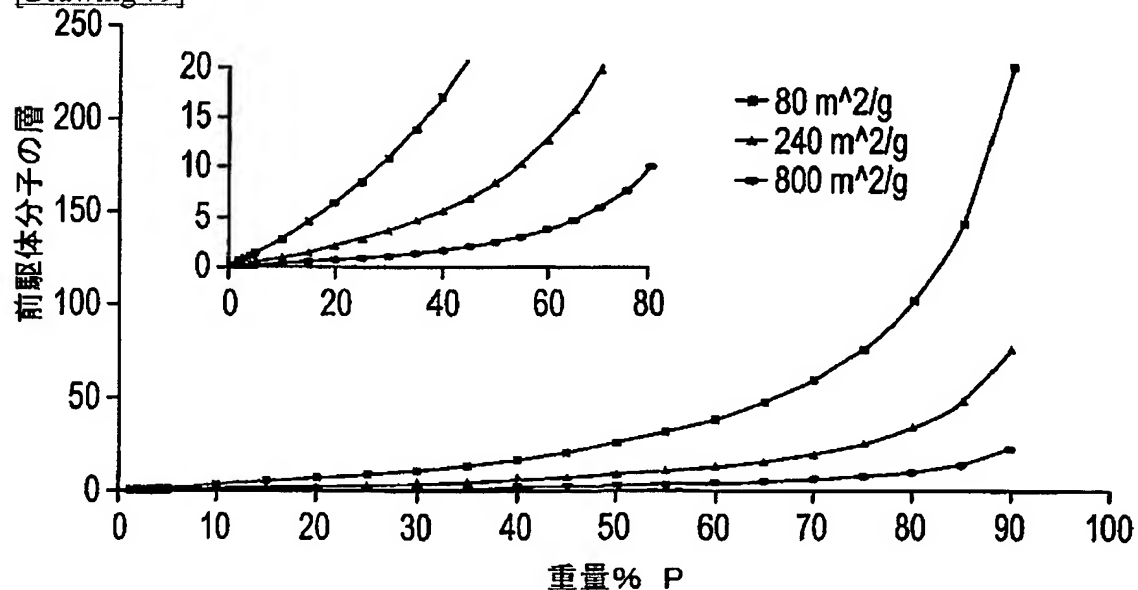
[Drawing 77]



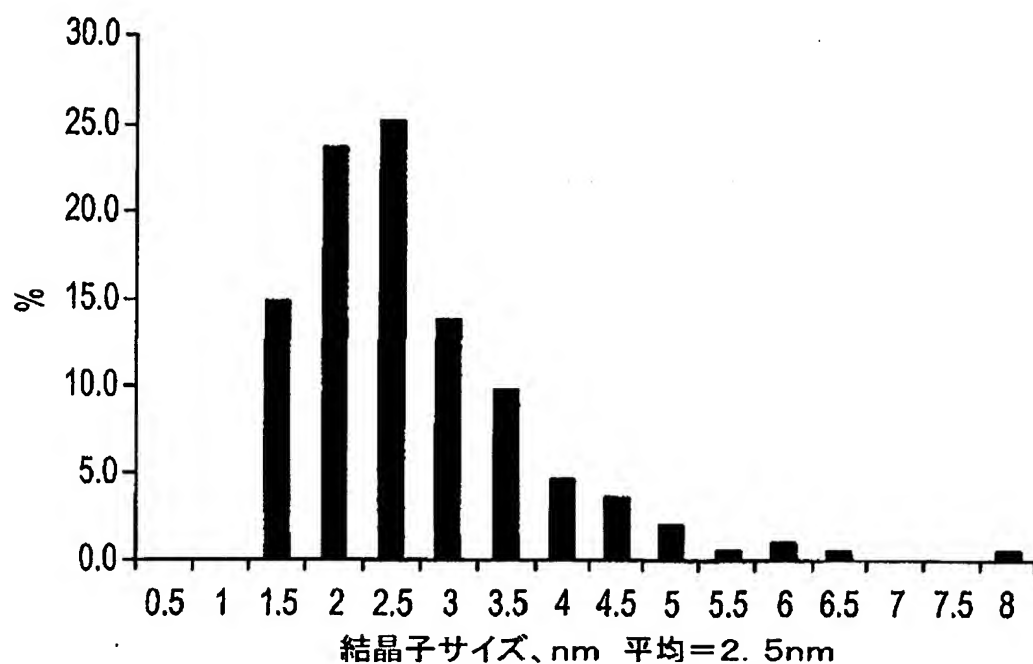
[Drawing 78]



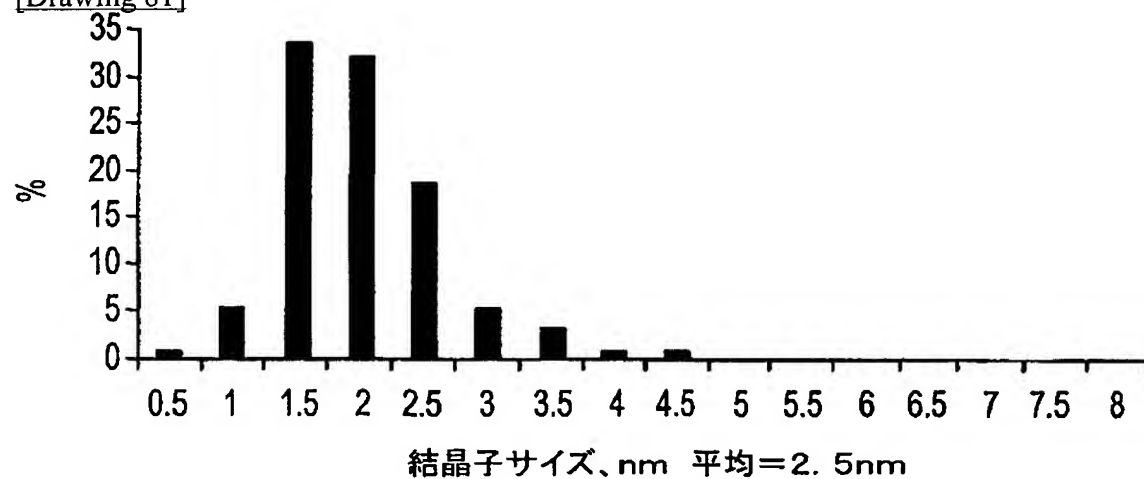
[Drawing 79]



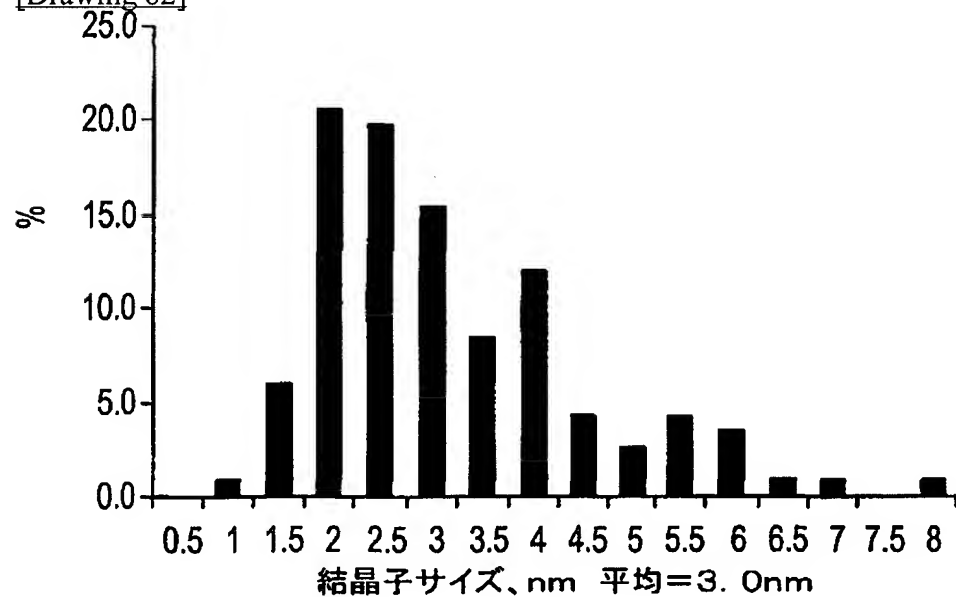
[Drawing 80]



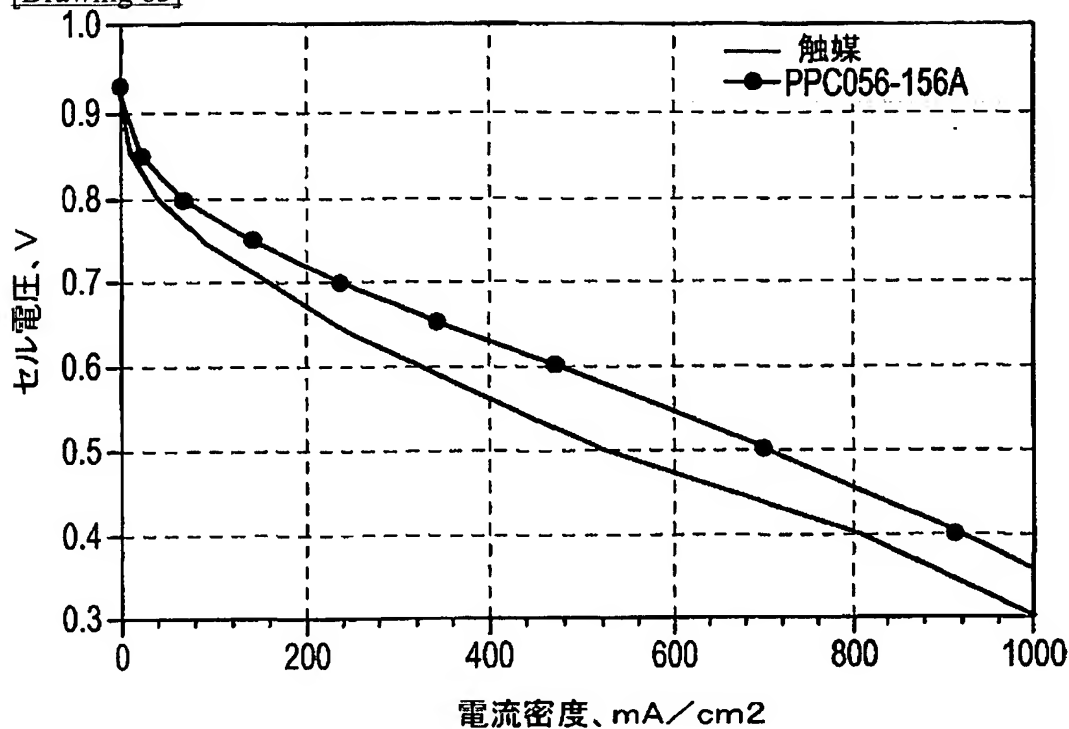
[Drawing 81]



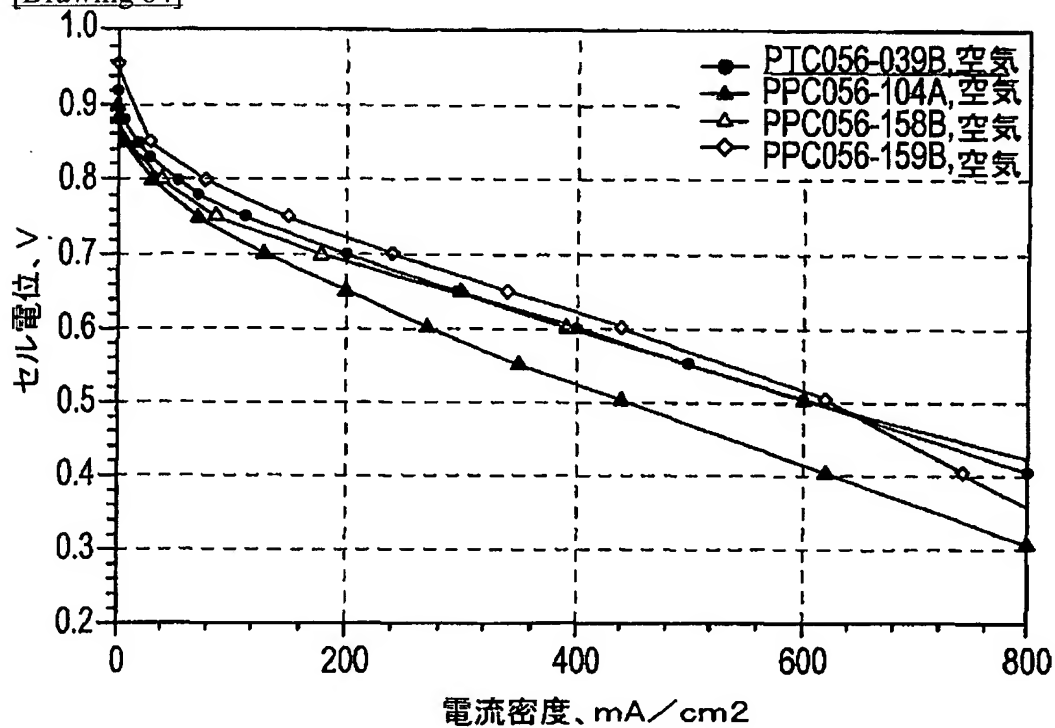
[Drawing 82]



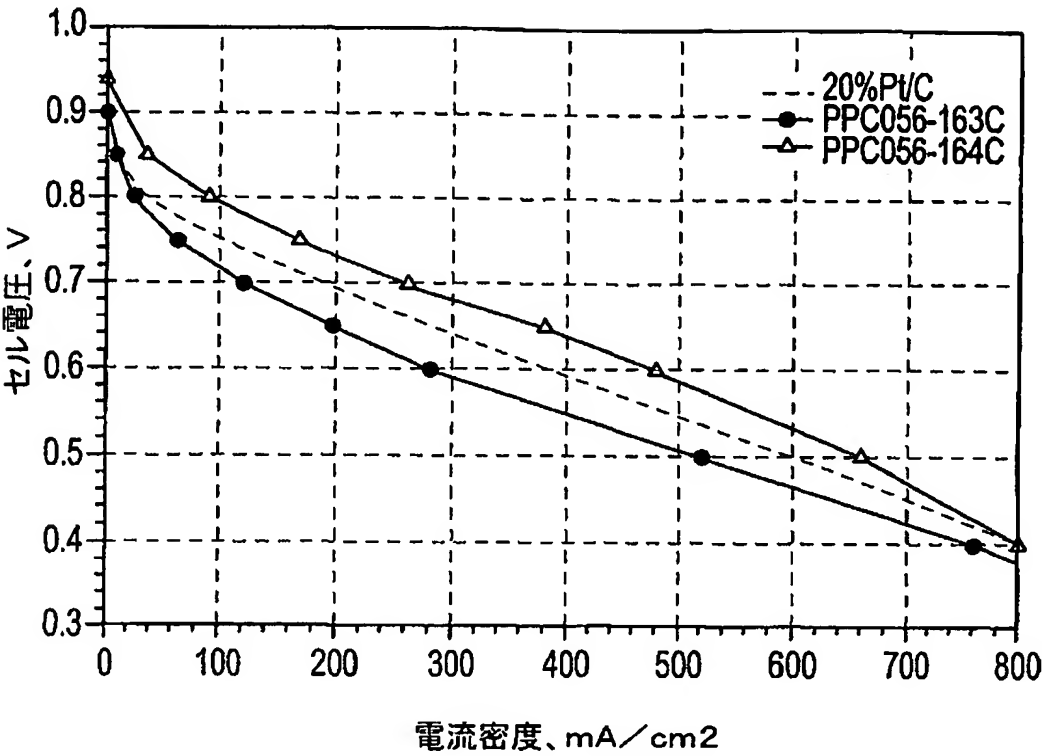
[Drawing 83]



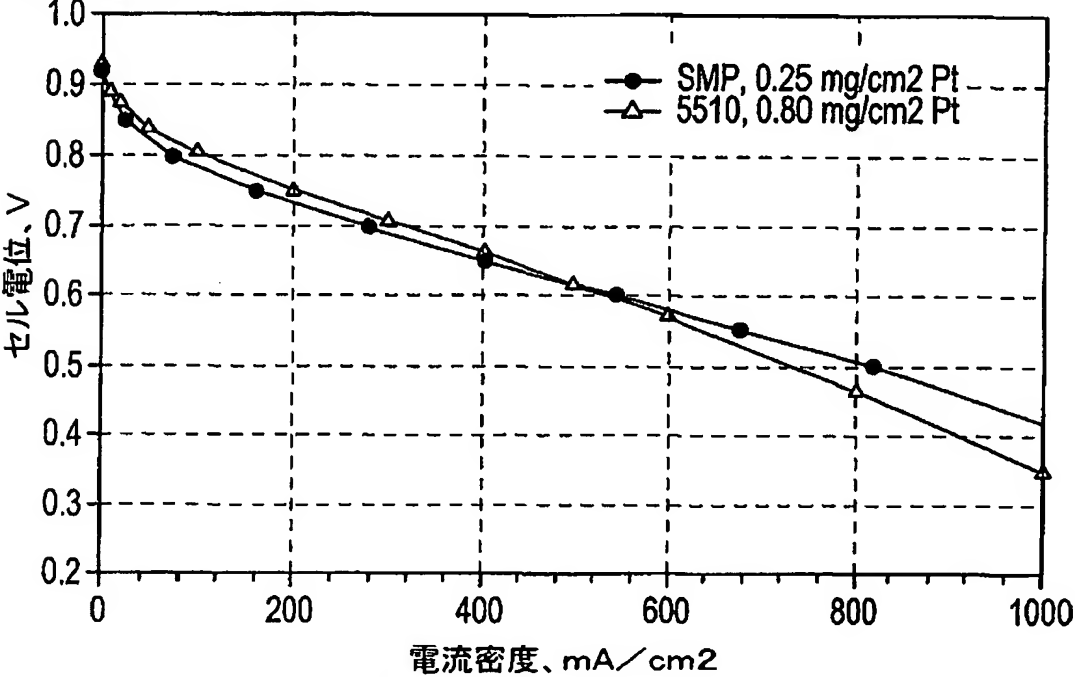
[Drawing 84]



[Drawing 85]



[Drawing 86]



[Drawing 87]

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3. In the drawings, any words are not translated.

## CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by the convention of 2 of Article 17 of Patent Law  
 [Section partition] The 1st partition of the 7th section  
 [Publication date] November 17, Heisei 17 (2005. 11.17)

[Official announcement number] \*\* table 2003-527735 (P2003-527735A)  
 [Official announcement day] September 16, Heisei 15 (2003. 9.16)  
 [Application number] Application for patent 2001-568577 (P2001-568577)  
 [The 7th edition of International Patent Classification]

H01M 4/90  
 B01J 35/04  
 H01M 4/88  
 H01M 4/92  
 H01M 4/96  
 H01M 8/10  
 H01M 8/18  
 H01M 12/08  
 // H01M 12/06

## [FI]

H01M 4/90	M
H01M 4/90	X
B01J 35/04	Z
H01M 4/88	K
H01M 4/92	
H01M 4/96	B
H01M 4/96	H
H01M 4/96	M
H01M 8/10	
H01M 8/18	
H01M 12/08	K
H01M 12/06	F

[Procedure revision]  
 [Filing Date] April 26, Heisei 16 (2004. 4.26)  
 [Procedure amendment 1]  
 [Document to be Amended] Specification  
 [Item(s) to be Amended] 0333  
 [Method of Amendment] Modification  
 [The contents of amendment]  
 [0333]

The example of the pharmaceutical preparation for the syringe quantum regurgitation was generated as follows.  
 The metal oxide catalyst was mixed with TEFRON (trademark) powder to the weight ratio of 5:1, and,

subsequently to the inside of an alpha-terpineol, it distributed. The barrier layer consisted of 20 - 40% of the weight of solid content. The pharmaceutical preparation containing the metallic oxide mixed with the Teflon processing carbon black which it was similarly supported on carbon and was distributed in isopropanol for screen-stencil was prepared. The amount of solid content support of this pharmaceutical preparation was changed to 10 - 40% of the weight.

[Procedure amendment 2]

[Document to be Amended] Specification

[Item(s) to be Amended] 0423

[Method of Amendment] Modification

[The contents of amendment]

[0423]

The first experiment in air shows the thing with the important balance between temperature and time amount which a small field exists. If a catalyst is put to too much high temperature or too much low temperature long time, platinum will be coagulated in remarkable magnitude. This coagulum is exaggerated by existence of hydrogen. The comparison of sample PPC113121A and PPC113086B shows the reducing power of hydrogen. Although afterbaking of the sample PPC113086B was carried out at 250 degrees C and not being changed in air, platinum not only changed, but the magnitude of microcrystal was observed by max when the same powder was processed in hydrogen at 150 degrees C like PPC113121A. This originated in the platinum kind which is easy to move by the elevated temperature existing partially under existence of hydrogen. It was made difficult that this migratory kind narrowed after-treatment conditions. After treatment was abandoned once what the spray drier will solve the transformation problem of platinum for with the reducing agent could understand, when this kind was discovered by reference.

[Procedure amendment 3]

[Document to be Amended] Specification

[Item(s) to be Amended] 0430

[Method of Amendment] Modification

[The contents of amendment]

[0430]

The comparison with PPC056158B and PPC056159B is contribution of high surface area carbon support. It illustrates. The microcrystal of sample PPC056158B (VULCAN(trademark) XC-72) is half magnitude mostly compared with the thing of PPC056159B (SHAWINIGAN BLACK (trademark)). VULCAN (trademark) The surface area of XC-72 is SHAWINIGAN. It is 3 times as large as that of BLACK (trademark), and average microcrystal size is about 2/3.

[Procedure amendment 4]

[Document to be Amended] Specification

[Item(s) to be Amended] drawing 83

[Method of Amendment] Addition

[The contents of amendment]

[Drawing 83] Drawing showing the engine performance of the membrane electrode assembly by the operation gestalt of this invention.

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[Translation done.]

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